Waste material recycling: Assessment of contaminants limiting recycling

Pivnenko, Kostyantyn

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

Waste material recycling: Assessment of contaminants limiting recycling

Kostyantyn Pivnenko

PhD Thesis
June 2016

DTU Environment
Department of Environmental Engineering

Waste material recycling: Assessment of contaminants limiting recycling

Kostyantyn Pivnenko

PhD Thesis
June 2016

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Kostyantyn Pivnenko

Waste material recycling: Assessment of contaminants limiting recycling

PhD Thesis, June 2016

Address: DTU Environment
Department of Environmental Engineering
Technical University of Denmark
Bygningstorvet, Building 115
2800 Kgs. Lyngby
Denmark

Phone reception: +45 4525 1600
Fax: +45 4593 2850

Homepage: www.env.dtu.dk
E-mail: info@env.dtu.dk

Printed by: GraphicCo
June 2016

Preface

This PhD thesis is based on the seven scientific journal articles and manuscripts prepared in collaboration with internal and external partners. Each of the publications below is assigned a Roman numeral (I-VII), used for references in the text (e.g., Paper IV).

I Edjabou M., Jensen M., Götze R., **Pivnenko K.**, Petersen C., Scheutz C., Astrup T.F. (2015) Municipal solid waste composition: Sampling methodology, statistical analyses, and case study evaluation, *Waste Management* (36), 12-23

II **Pivnenko K.**, Eriksson E., Astrup T.F. (2015) Waste paper for recycling: Overview and identification of potentially critical substances, *Waste Management* (45), 134-142

III **Pivnenko K.**, Olsson M., Götze R., Eriksson E., Astrup T.F. (2016) Quantification of chemical contaminants in the paper and board fractions of municipal solid waste, *Waste Management* (51), 43-54

IV **Pivnenko K.**, Pedersen G.A., Eriksson E., Astrup T.F. (2015) Bisphenol A and its structural analogues in household waste paper, *Waste Management* (44), 39-47

V **Pivnenko K.,** Eriksen M.K., Martín-Fernández J.A., Eriksson E., Astrup T.F. (2016) Recycling of plastic waste: Presence of phthalates in plastics from households and industry, *Waste Management*, In press

VI **Pivnenko K.**, Granby K., Eriksson E., Astrup T.F. Recycling of plastic waste: Screening for brominated flame retardants, *Manuscript*

VII **Pivnenko K.**, Laner D., Astrup T.F. Material cycles and chemicals: Dynamic material flow analysis of contaminants in paper recycling, *Submitted*

In this online version of the thesis, **Paper I-VII** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Bygningstorvet, Building 115, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk.

Additionally following two journal publications, one report and several contributions to conference proceedings or workshops have been done within scope of the PhD project (arranged in descending chronological order):

Götze R., **Pivnenko K.**, Boldrin A., Scheutz C., Astrup T.F. (2016) Physico-chemical characterization of material fractions from residual and source-segregated household waste in Denmark, *Waste Management*, In press

Pivnenko K., Astrup T.F. (2016) The challenge of chemicals in material cycles, *Editorial for Waste Management,* In press

Pivnenko K., Astrup T.F. (2015) Chemical contamination of material cycles, in: Abstract Book - *DTU Sustain Conference 2015*. Technical University of Denmark, Kgs. Lyngby, Denmark

Pivnenko K., Jakobsen L.G., Eriksen M.K., Damgaard A., Astrup T.F. (2015) Challenges in plastics recycling, in: Cossu, R., He, P., Kjeldsen, P., Matsufuji, Y., Reinhart, D., Stegmann, R. (Eds.), *Proceedings of the Fifteenth Waste Management and Landfill Symposium, Sardinia 2015*. CISA Publisher, S.Margherita di Pulia, Sardinia, Italy

Pivnenko K., Eriksson E., Astrup T.F. (2015) Chemicals in material cycles, in: Cossu, R., He, P., Kjeldsen, P., Matsufuji, Y., Reinhart, D., Stegmann, R. (Eds.), *Proceedings of the Fifteenth Waste Management and Landfill Symposium, Sardinia 2015*. CISA Publisher, S.Margherita di Pulia, Sardinia, Italy

Edjabou V.M.E., **Pivnenko K.**, Petersen C., Scheutz C., Astrup T.F. (2015) Compositional data analysis of household food waste in Denmark. Abstr. from *6th International Workshop on Compositional Data Analysis.* L'Escala, Girona, Spain

Pivnenko K., Astrup T.F. (2014) Material recycling: Presence of chemicals and their influence on the circular economy concept, in: Abstract Book - *DTU Sustain Conference 2014.* Technical University of Denmark, Kgs. Lyngby, Denmark

Pivnenko K., Eriksson E., Astrup T. F. (2014) Source and hazard identification of substances in bio-liquid from the REnescience technology. *Report for DONG Energy*, Fredericia, Denmark

Pivnenko K., Eriksson E., Astrup T.F. (2014) Polychlorinated biphenyls (PCBs) in waste paper from Danish household waste, in: Abstract from *5th International Conference on Engineering for Waste and Biomass Valorisation*. Rio de Janeiro, Brazil

Pivnenko, K., Eriksson, E., Astrup, T.F., 2013. Presence of potentially critical substances in waste paper, in: R. Cossu, P. He, P. Kjeldsen, Y. Matsufuji, D. Reinhart, R. Stegmann (Eds.), *Proceedings of the Fourteenth Waste Management and Landfill Symposium, Sardinia 2013*. CISA Publisher, S.Margherita di Pulia, Sardinia, Italy

Astrup, T.F., Scheutz, C., Damgaard, A., Boldrin, A., Rørbech, J.T., Vyzinkarova, D., Klinglmair, M., Edjabou, V.M.E., Götze, E., Allegrini, E., **Pivnenko, K.**, 2013. Integrated resource management and recovery (IRMAR): a new Danish initiative, in: Cossu, R., He, P., Kjeldsen, P., Matsufuji, Y., Reinhart, D., Stegmann, R. (Eds.), *Proceedings of the Fourteenth Waste Management and Landfill Symposium, Sardinia 2013*. CISA Publisher, S.Margherita di Pulia, Sardinia, Italy

Acknowledgements

Neither the document you are reading right now, nor the work leading to it could be possible without intentional or sometimes even non-intentional help from so many people. Some of the prominent ones I would like to thank here.

Thomas F. Astrup, as the main supervisor, offered me an opportunity to embrace myself on a journey full of discoveries, challenges, knowledge, frustrations and accomplishments. His careful, polite and constructive guidance helped moderating my ambitions, keeping me focused and maintaining the spirits high. *Eva Eriksson*, as the co-supervisor, gave practical guidance with a personal touch and helped me navigate in the labyrinth of the chemical world. Internal and external (*David, Gitte, Martin and Kit*) co-authors showed exceptional understanding and provided their expertise whenever it was required.

Thanks to those who created my ever-lasting warm feelings about the department (*Carson, Denisa, Elham, Fabio, Ioannis, Mike, Pedram, Rene and Uli*) and residual resources section (*Elisa, Line, Morten, Ramona, Stefania, Veronica, Vincent and Yoshi*) within it. Thank you *Ramona, Vero* and *Vincent* for being there from the first moment, engaging in countless discussions, pretending to compete and hopefully remaining friends beyond the PhD, university and Denmark. Thank you *Rosemary* for providing shelter at home and in heart and occasionally teaching life lessons that I will never forget.

I would like to express my exceptional gratitude towards *Elena*, for being the catalyst for happiness and assimilation of the lessons learned. Thank you *Ilias* for giving your best and making sure I kept myself fed and healthy. Beyond all I would thank my mother, who always inspired me and would always serve as the reference point for unconditional love and support.

Summary

Materials and articles are constantly increasing in their complexity, promoted by demand for functionality, appearance and cost of consumer and industrial products. To satisfy these demands, a variety of chemicals and combinations of materials are used in products. On the other hand, material recycling has been recognised as a backbone of circular economy, with constant measures and initiatives being proposed in order to increase the recycling rates of materials being consumed.

Material cycles are complex and dynamic systems where chemicals are added and removed in production, manufacturing, consumption and waste management stages within a product's lifecycle (Figure 1). Hence, waste materials contain potentially hazardous chemicals that are unwanted in the new products made of the recycled raw materials. So far, the presence of such chemicals in materials for recycling has not been systematically investigated. This PhD project provided detailed quantitative data following a consistent approach to assess potential limitations for the presence of chemicals in relation to material recycling. Paper and plastics were used as illustrative examples of materials with well-established recycling schemes and great potential for increase in recycling, respectively.

The approach followed in the present work was developed and performed in four distinct steps. As step one, **fractional composition** of waste paper (30 fractions) and plastics (9 fractions) from households in Åbenrå municipality (Southern Denmark) was provided. In step two, a **literature review** concerning presence of chemicals in paper was performed. It was shown that approx. 10,000 individual chemicals may be present in paper products. Among the chemicals identified, approx. 150 were considered hazardous and approx. 50 were identified as particularly relevant with respect to paper recycling. Potential sources for chemicals in paper were evaluated. Printing and conversion were identified as the most important steps in relation to paper cycle, but chemicals added non-intentionally (NIAS) in a variety of steps (Figure 1) may also play a role.

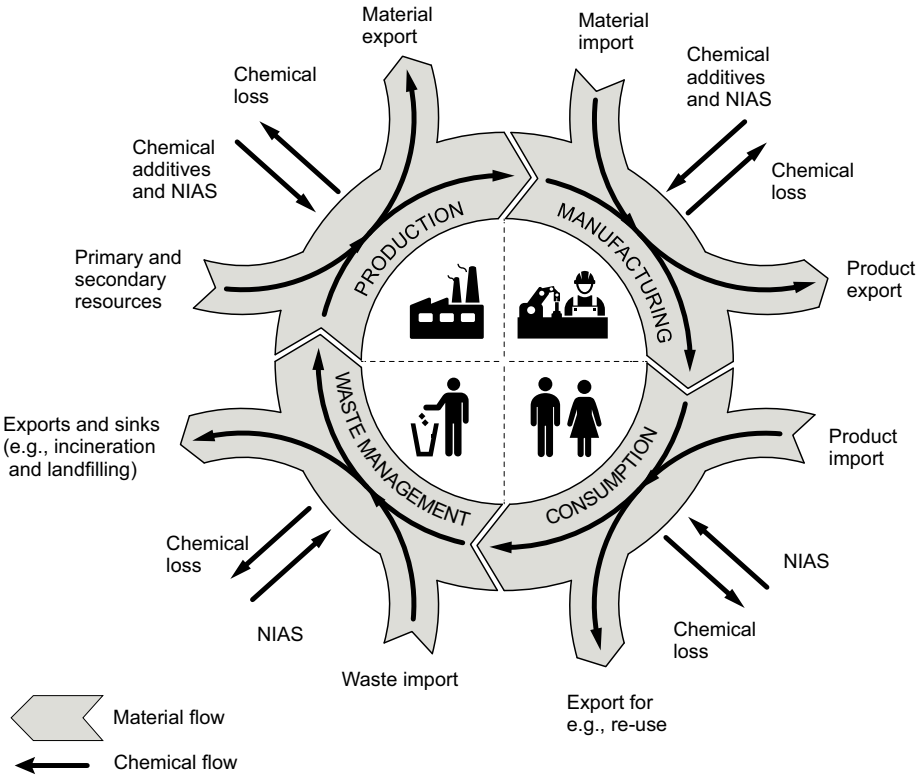


Figure 1 Schematic representation of generic material and chemical cycles for a defined geographical boundary (e.g., Europe). Chemical loss implies evaporation, degradation, migration, etc., as well as removal through material (re) processing. NIAS: Non-Intentionally Added Substances [1].

Following, **chemical analyses** for quantification of a range of potential contaminants in paper (mineral oils, phenols, phthalates, polychlorinated biphenyls and toxic metals) and plastics (phthalates and brominated flame retardants) were done. The results indicated large variations in presence of chemical contaminants (from µg/kg to g/kg), depending on the contaminant in focus or the sub-fraction (e.g., books) of the material fraction being analysed (e.g., paper). Certain material fractions showed higher content of chemicals (e.g., bisphenols in thermal paper and flame retardants in polystyrene plastics), potentially detrimental to their recycling. Finally, a **material flow analysis (MFA)** approach revealed the potential for accumulation and spreading of contaminants in material recycling, on the example of the European paper cycle. Assessment of potential mitigation measures indicated that prevention of chemical use, removal of chemicals in recycling and constrain chemicals to specific product flows were in decreasing order of effectiveness. The assessment also pointed out the potential trade-offs between material quantity (i.e. recycling rates) and quality (i.e. presence of contaminants) when mitigation measures are applied.

Dansk sammenfatning

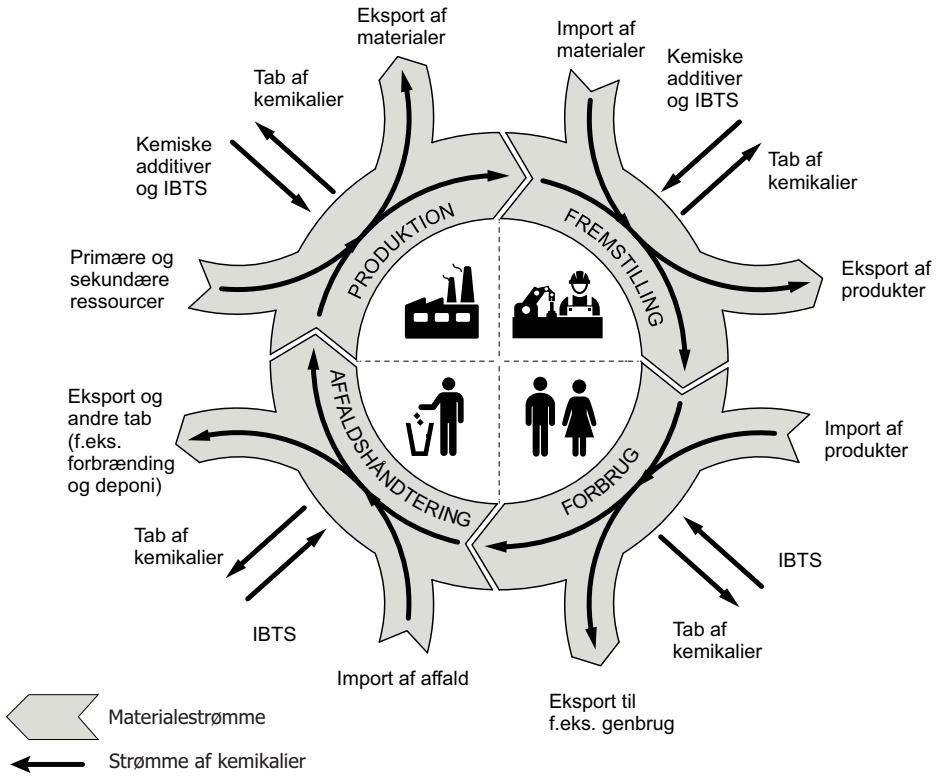
Kompleksiteten af materialer og produkter vokser konstant, drevet frem af krav til funktionalitet, udseende og omkostninger af forbruger- og industrielle produkter. For at imødekomme disse krav anvendes en lang række forskellige kemikalier og kombinationer af materialer i vores produkter. Genanvendelse er på den anden side anerkendt som et vigtigt element i tilvejebringelsen af nye råmaterialer til industrien såvel som ønsket om at lukke materialekredsløb i samfundet, f.eks. i relation til nye initiativer inden for cirkulær økonomi.

Materialekredsløb er komplekse og dynamiske systemer, hvor kemikalier tilsættes og fjernes i de forskellige faser af produkternes livscyklus: produktion, fremstilling, forbrug og affaldshåndtering (Figur 1). Dermed indeholder affaldsmaterialer potentielt kemikalier, som er uønskede i nye produkter baseret på genanvendte råmaterialer. Indtil nu er tilstedeværelsen af sådanne kemikalier i genanvendelige materialer ikke blevet systematisk undersøgt. Dette PhD projekt har tilvejebragt detaljerede, kvantitative data ud fra en konsistent metode til vurdering af potentielle begrænsninger ved tilstedeværelsen af kemikalier i relation til materialegenanvendelse. Papir og plast blev anvendt som illustrative eksempler på materialer med et veletableret genbrugssystem henholdsvis et stort potentiale for øget genanvendelse.

Metoden består af fire separate trin. Første trin omfattede en fastlæggelse af den **fraktionsvise sammensætning** af prøver af papir- (30 fraktioner) og plastaffald (9 fraktioner) indsamlet fra husstande i Åbenrå Kommune. I trin andet blev et **litteraturstudie** gennemfart for at afdække tilstedeværelsen af kemikalier i papir. Det blev demonstreret, at ca. 10.000 individuelle kemikalier kan være til stede i papirprodukter. Af de identificerede kemikalier blev ca. 150 betegnet som problematiske og omkring 50 kemikalier vurderet som specifikt relevante i relation til genbrug af papir. Potentielle kilder til kemikalier i papir blev evalueret. Trykning og konvertering blev identificeret som de vigtigste trin materialekredsløbet for papir, men kemikalier som ikke bevidst tilsættes (IBTS) som en del af de industrielle processer spiller muligvis også en rolle.

Som et tredje trin blev foretaget **kemiske analyser** for at kvantificere udvalgte stoffer i papir (mineralske olier, fenoler, ftalater, polyklorinerede bifenoler og toksiske metaller) og plast (ftalater og bromerede flammehæmmere). Resultaterne viste store variationer i den kemiske forurening af materialerne (fra µg/kg til g/kg), afhængig af det specifikke kemiske stof og underkategorien

(f.eks. bøger) af den materialefraktion, der blev analyseret (f.eks. papir). Visse materialefraktioner havde et højere indhold af kemikalier (f.eks. bisfenol i bon-papir og flammehæmmere i polystyren plast), som potentielt kan udgøre et problem for genanvendelse.



Figur 1. Skematisk fremstilling af generelle cyklus for materialer og kemikalier for et afgrænset geografisk område f.eks. Europa. Tab af kemikalier omfatter fordampning, nedbrydning, migration osv., samt fjernelse gennem materiale-oparbejdning og -genanvendelse IBTS: Ikke-bevidst tilsatte stoffer [1].

Med det europæiske papirkredsløb som eksempel, blev i fjerde trin gennemført en **massestrømsanalyse (MFA)** for kvantificering af potentialet for akkumulering og spredning af forurenende stoffer ved papirgenanvendelsen. En vurdering af potentielle afhjælpende initiativer indikerede, at forebyggelse af kemikalieforbruget i industrien var det mest effektive initiativ til fjernelse af kemikalier i papirprodukter, mens øget rensning af returpapir i industrien og selektiv sortering og genanvendelse af papir fraktioner var mindre effektive initiativer. Vurderingen fastlagde desuden de potentielle trade-offs mellem kvantitet i genanvendelsen (dvs. genanvendelsesprocenter) og kvalitet (dvs. tilstedeværelsen af kemikalier og renheden af produkterne) ved de udvalgte initiativer.

Table of contents

Abbreviations

ABS	Acrylonitrile butadiene styrene
BFR	Brominated flame retardant
BPA	Bisphenol A
BPB	Bisphenol B
BPE	Bisphenol E
BPF	Bisphenol F
BPS	Bisphenol S
DBP	Dibutyl phthalate
DEHP	Bis (2-ethylhexyl) phthalate
DiBP	Di-iso-butyl phthalate
HBCD	Hexabromocyclododecane
HDPE	High-density polyethylene
HMW	Height molecular weight
HPP	4-cumylphenol
LDPE	Low-density polyethylene
LMW	Low molecular weight
LOD	Limit of detection
MFA	Material flow analysis
MOH	Mineral oil hydrocarbon
NCR	Non-carbon copy paper
NIAS	Non-intentionally added substances
PCB	Polychlorinated biphenyl
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SFA	Substance flow analysis
TBBPA	Tetrabromobisphenol A
2,4-DBP	2,4-dibromophenol
2,6-DBP	2,6-dibromophenol
2,4,6-TBP	2,4,6-tribromophenol

1 Introduction

1.1 Background

Concept of linear production (extract-convert-use-discard), applied massively from the times of industrial revolution, has created a lot of scepticism in the world of limited resources. As an alternative, sustainable production concept was proposed in the late 1980s [2]. The backbone of the concept was to pursuit a circular production, where ideally all materials are extracted, converted into products, used by consumers, and discarded, are recovered, processed, and converted into newly manufactured products - thus closing the material loop. Major advantages associated with material recirculation (i.e. recycling) include reduced dependency on natural resources and non-renewable energy sources, as well as potential reduction in our environmental footprint [3]. Beneficial as it may seem from our current sustainability point of view, the case might be oversimplified.

Ever-growing demands towards performance, durability, appearance, etc. of materials and products in the anthroposphere has led to increase in their complexity. These potential improvements are predominantly achieved through use of chemical additives. As an example, flame-retardants reduce fire risks for electrical equipment and furniture [4], polymeric resins improve durability of paper [5], antioxidants increase life span of plastics [6], fragrances, inks and pigments increase product's appeal to a consumer. Addition of chemicals may improve functionality of a product or the production process itself. Most of the chemicals are intentionally added by an industry, while non-intentionally added chemicals (generally referred to as NIAS) commonly result from chemical impurities, as well as reaction and degradation products of chemicals intentionally used [7].

Once obsolete products and commodities are discarded and recovered for recycling, they bring along chemicals they might contain. When waste products are re-processed, chemicals may persist and accumulate or spread into newly manufactured products. This is of particular concern when applications and uses of products before and after recycling are different (i.e. open loop recycling [8]), and chemical - sensitive application are concerned. As an example, food packaging made of recycled materials has been shown to contain chemical contaminants with potential for migration into foodstuff [9]. Additionally, material recycling facilities have shown potential to release chemicals into the environment, constituting them as a source of contamination

[10,11]. Hence, presence of chemicals may jeopardize the quality of products based on recycled materials and can potentially put the human health and the environment at unnecessary risk.

Paper and plastics are prominent examples of materials either being well-established in their recycling or having a great potential for increased recycling rates, respectively. Recycling rates of paper reached 58% globally and 72% in Europe, while content of recycled fibres in selected paper product groups (e.g., newsprint and board packaging) may reach as high as 95% [12,13]. In contrast, only 26% of the European post-consumer plastics were recycled in 2012 [14]. However, technological developments in waste plastics management and ambitious recycling goals set by recent European legislation promote recycling of plastics with 65% of municipal and 75% of packaging waste (including plastics) expected to be recycled by 2030 [15–17].

1.2 Aim of the PhD project

The overall objective of the PhD project was to develop and apply a scientifically based approach for assessing the limitations for recycling based on the presence of contaminants in the waste materials. This was done by focusing on paper and plastics as prominent examples of recyclable materials. Specific objectives include: i) provide fractional composition of paper and plastics in residual and source-segregated household waste; ii) review literature and perform hazard identification of chemicals in paper material and products; iii) quantify selected hazardous chemicals in samples of paper and plastics; iv) evaluate contaminant accumulation and potential mitigation measures within the European paper cycle.

1.3 Content of the PhD thesis

Materials and methods (Chapter 2)

After description of the general approach followed in this work and the experimental approach for material sampling and pre-treatment (Paper I), principles behind literature review, hazard identification and prioritization of chemicals in paper are provided. Next, chemical analyses performed on paper and plastics are briefly described. Finally, the modelling methodology used for evaluation of potential impacts presence of chemical contaminants may have on material cycles is defined.

Literature review (Chapter 3)

Provides an overview of the state-of-the-art literature on presence of chemicals in paper, while identifying the priority chemicals with potential for paper cycle contamination (Paper II).

Chemicals in recyclables (Chapter 4)

Presents and discusses the main results from the analytical quantification of the selected priority chemicals in the collected samples of paper (Paper III and IV) and plastics (Paper V and VI).

Material cycles (Chapter 5)

Elaborates on presence of chemicals in material cycles while showing potential for accumulation and spreading of chemicals in the European paper cycle. Additionally, assessment of potential measures to mitigate "chemical cycling" is provided (Paper VII).

Conclusions (Chapter 6)

Concludes the work and provides the main outcomes based on results and discussion provided in Chapters 2-5.

Recommendations and perspectives (Chapter 7)

Finally, provides recommendations towards the stakeholders in a material value chain and gives an outlook on the perspectives for future work.

2 Materials and methods

2.1 Overview of the approach followed

The work provides a combination of material sampling, literature review, chemical analyses and flow modelling in order to fulfil the aims of the project. Samples of paper and plastics were obtained for chemical analyses and to provide quantitative data on presence of selected priority chemicals in the materials in focus. Literature review was performed for paper in order to provide an overview of chemicals potentially present in paper as material and create basis for selecting chemicals for analyses through a hazard identification procedure. This was followed by chemical analyses, where selected hazardous chemicals were quantified in the collected samples of paper and plastics. Finally, based on the quantitative data previously obtained, the potential effects of chemical presence on recycling were assessed on the example of paper. The overall activities were divided in four distinct steps, with details from each of the steps provided in the following sections (2.2 – 2.5):

i) Material sampling and pre-treatment (paper and plastics)

ii) Literature review and hazard identification (paper)

iii) Chemical analyses (paper and plastics)

iv) Assessment of chemicals in material cycles (paper)

2.2 Material sampling and pre-treatment

2.2.1 Waste materials

Schematic representation of the waste paper and plastics sampling and pre-treatment procedure is provided in Figure 2-1. Household waste was sampled in the Åbenrå municiplaity in the Southern Denmark. The sampling was perfomed in April 2013, in accordance with standard method for solid waste sampling [18]. The samples represented both residual and source-segregated waste material fractions of the waste generated by 100 single-family households within the period of two weeks. Paper and plastics in the residual waste material flow were collected and disposed off together with other solid waste materials (e.g., kitchen waste), while source-segregated waste was sorted into a single flow intended for recycling. Details on the sampling campaign are provided in Paper I and III.

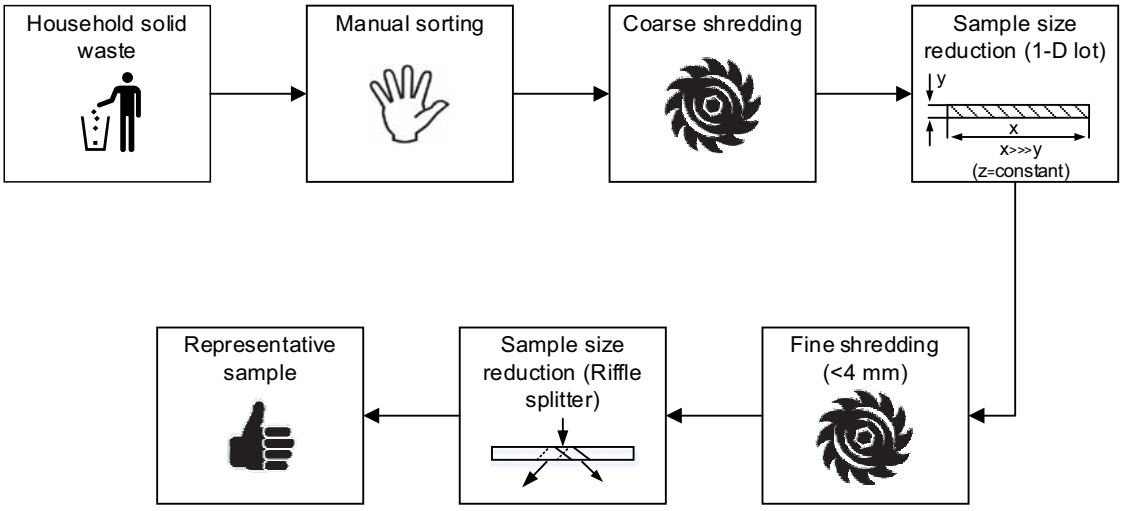


Figure 2-1 Schematic representation of waste material sampling and pre-treatment (Paper III).

After being collected, samples of waste paper and plastics were manually sorted into a catalogue of waste material fractions with three levels of details (Paper I). Waste paper was sorted according to the physical appearance of the paper items (e.g., newspapers, corrugated boxes) and their potential use (e.g., food packaging). Waste plastics, on the other hand, were sorted into fractions according to the resin identification code (ASTM D7611/D7611M) marked on each of the items (e.g., 1 – PET and 2 - HDPE). A tiered approach in definition of waste material fractions provides detailed data of waste composition while allowing direct comparison between datasets with different needs for sorting and data aggregations. After manual sorting, each of the separate paper and plastics fractions was stored in paper sacks before the coarse shredding (ARP SC2000, Brovst, Denmark). The mass of material for coarse shredding was limited to approx. 40 kg. Larger fractions (e.g., newspapers) were reduced in size through randomly selecting the sacks with sample to be shredded. The coarse shredding was followed by a one-dimension (1-D) lot size reduction [19]. In brief, coarsely shredded waste samples were arranged into a line (width = approx. 40 cm, maximum length = approx. 400 cm, and height = approx. 5 cm (y, x and z in Figure 2-1, respectively)) and subsequent increments were taken using a plastic box (Figure 2-2). Half of the increments were discarded while the other half were rearranged into a new line and the process was repeated until approx. 0.5 to 2.0 kg (depending on the material density) of sample were obtained. Then samples were finely shredded (SM2000, Retsch, Germany) down to particle size of ≤ 4 mm. To increase material brittleness and prevent malfunction of the equipment samples of plastics were treated with liquid nitrogen before being shredded. Finally, size reduction using a riffle

splitter (10 x 2 cm chutes) was performed, in order to obtain the final samples for analyses. In order to avoid losses of contaminants in focus, shredded waste paper samples were lyophilised (CoolSafe, Lynge, Denmark) and stored in glass jars (maximum volume of 1 L) at -20 °C. Samples of plastics would not be subjected to chemical analyses for volatile substances, thus being dried at 105 °C for 24 hours and stored in plastic (polyethylene terephthalate (PET)) containers at room temperature in a dark and dry environment.

Figure 2-2 One dimension (1-D) lot size reduction illustrating 1-D lot of a coarsely shredded waste paper fraction, an increment taken and a plastic box used for taking subsequent increments.

2.2.2 Other (non-waste) materials

In addition to samples of waste materials, selected paper products (i.e. thermal paper receipts, non-carbon copy paper (NCR) and printer paper) were sampled for analyses. Samples of thermal paper receipts (n=13) were obtained from a variety of business establishments (e.g., super market, gas station, grocery store, clothing retailer, coffee shop) of the Copenhagen Capital Area of Denmark in October 2014. Samples of NCR paper were purchased online, while samples of printer paper were obtained from an authorized local retailer. Thermal paper samples were directly shredded in a conventional office paper shreeder (Powershred MS-450CS, Fellows, USA) down to 2 x 8 mm pieces,

lyophilised (CoolSafe, Lynge, Denmark) and stored at -20 °C prior to analysis. Further description of paper product samples and their pre-treatment are provided in Paper IV.

Furthermore, samples of processed plastics (i.e. virgin and recycled plastics) were obtained directly from plastic producers and recyclers in China, Denmark, Germany, and the Netherlands. The obtained samples were not intended to cover the variations in presence of chemical contaminants in plastics on the global market, but provide an illustration of potential differences and offer the first basis for evaluation of plastic contamination. Samples included plastics of common resin types (e.g., PET, HDPE, LDPE, PP) either of primary (virgin) or secondary (recycled) production. In total 28 samples of plastics were collected from industry, details on which can be obtained from Paper VI. The samples of plastics were received in form of granules, flakes or pellets, and were considered homogeneous due to the nature of their production (Figure 2-3). Thus, in contrast to the samples of household waste plastics, samples of processed plastics did not undergo additional pre-treatment (e.g., sample size reduction and splitting) before being used for chemical analyses.

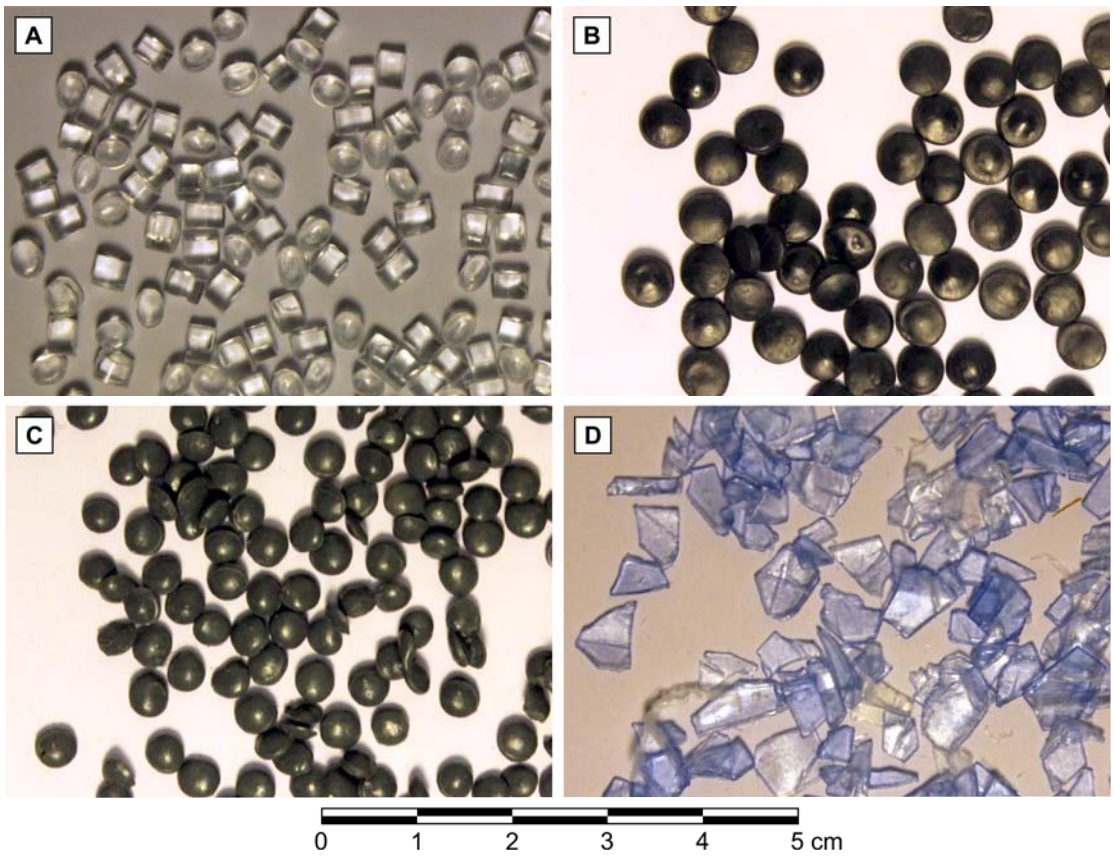


Figure 2-3 Illustration of selected samples of processed plastics; A) virgin PS; B) recycled HDPE; C) recycled PP; D) recycled PET.

2.3 Literature review and hazard identification

Schematic view of the procedure involved in the literature review and hazard identification of chemicals potentially present in paper material is provided in Figure 2-4. Details on the selection of data sources, their description and further details of the criteria for identifying potential priority chemicals are provided in Paper II.

As **first step**, available literature was reviewed and chemicals either used by the industry (i.e. paper production, conversion or printing) or identified in paper through chemical analyses were selected. Data on chemicals in paper was retrieved from a variety of sources including national product registries, scientific assessments, reports, inventories and regulations. The overview of the data sources used and their contribution to the list of chemicals compiled in the first step is presented in Table 2-1. To avoid double-counting and ambiguity, only chemicals that could be assigned a valid CAS number were included in the study.

In the **second step**, chemicals classified as hazardous in accordance to the European REACH regulation [20] were identified and selected. In order to be selected, chemicals had to be classified in either of the following six hazard classes: i) carcinogenicity (Carc. 1A or 1B); ii) germ cell mutagenicity (Muta. 1A or 1B); iii) reproductive toxicity (Repr. 1A or 1B); iv) persistent, bioaccumulative and toxic (PBT); v) very persistent and very bioaccumulative (vPvB); vi) endocrine disrupting chemicals (EDCs). Due to lack of publicly available data, chemicals with incomplete hazard profile were not selected in the present step, potentially leading to underestimation in the number of chemicals finally selected.

In the **third step**, by using selected inherent properties and fate constants of the chemicals (e.g., K_{oc}: partition coefficient between organic carbon and water), the ones associated with paper fibres and potentially persisting paper re-processing were identified, based on a methodology described by Baun et al. [21].

Finally, in the **fourth step** the selected chemicals were assessed in accordance with their biodegradability and classified into persistent, inherently, and readily biodegradable. This step was based on experimental scientific literature or biodegradability models and relevance to particular processes in paper recycling was not established.

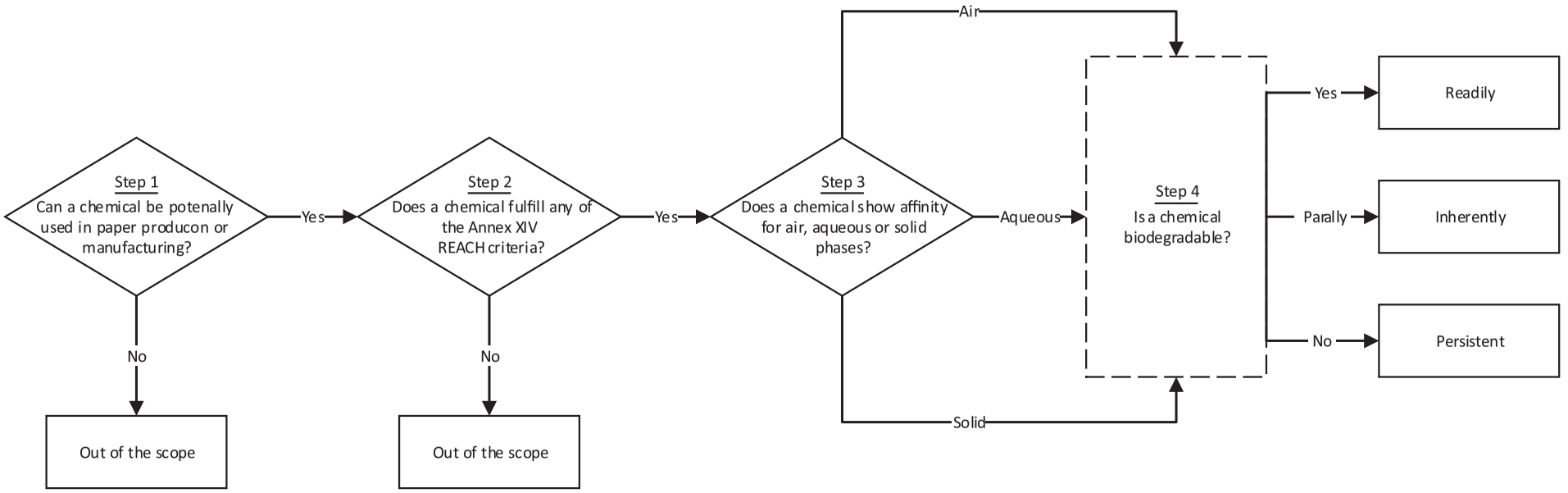


Figure 2-4 Schematic representation of the methodology applied in selecting relevant chemicals of interest (Paper II).

Table 2-1 Data sources used in the study and their quantitative contribution to list of chemicals (Paper II).

Source	Number of chemicals	Description	Industry	Ref.
Literature	348	Scientific literature providing analytical data on the identification or quantification of chemicals in paper and/or board	Paper and paper product manufacturing, and NIAS	[9,22–45]
Danish product register	75	Chemicals used in preparations of articles. Danish industry for pulp, paper and paper products	Paper and paper product manufacturing	[46]
Swedish product register	144	Chemicals used in preparations of articles. Swedish industry for pulp, paper and paper products	Paper and paper product manufacturing	[47]
Danish EPA	415	Inventory of chemicals used by the Danish printing industry	Paper product manufacturing*	[48]
RiskCycle	12	Database of chemical additives used in paper production	Paper manufacturing	[49]
ZELLCHEMING[1]	44	Chemical additives for the production of pulp and paper	Paper manufacturing	[5]
EFSA[2]	223	Chemicals currently used in the manufacture of paper and board	Paper manufacturing	[50]
FDHA[3]	4575	Chemicals permitted to be used in the manufacture of packaging inks	Paper product manufacturing*	[51]
EuPIA[4]	3858	Inventory list of chemicals used in the manufacture of food packaging inks	Paper product manufacturing*	[52]
TOTAL:	9694	-	-	-

[1]Vereins der Zellstoff und Papier Chemiker und ingenieure (German for: Association of Chemical Pulp and Paper Chemists and Engineers); [2]European Food Safety Authority; [3]Swiss Federal Department of Home Affairs; [4]European Printing Ink Association.*not limited to paper matrix

2.4 Chemical analyses

Chemical analyses performed in this work, the equipment used and the sources for further details are summarised in Table 2-2. Few of the analytical methods used had standardised procedure to be followed, hence most of them were based on the available standards and literature, adopted to and tested on the respective materials before being applied. Analysis of phthalates in plastics (Paper V) was accompanied by certified reference material (NMIJ CRM 8151-a, National Metrology Institute of Japan). Recoveries obtained were 141±6 %, 90±5 %, and 99±2 % for dibutyl phthalate (DBP), butyl benzyl phthalate (BBP) and bis (2-ethylhexyl) phthalate (DEHP), respectively. All the included analyses were accompanied with reference methods for quality assurance (e.g., use of blanks, analyses on replicates, recovery based on spiking), details on which can be found in the respective publications (Paper III, IV, V and VI).

Table 2-2 Overview of chemical analyses performed on paper and plastics.

#	Chemical group	Analytes	Equipment used*	Further details
PAPER	Mineral oil hydrocarbons	nC_{10}-nC_{20}, nC_{20}-nC_{30}, nC_{30}-nC_{40}	GC-FID	Paper III
	Phenols	Nonylphenol (NP)[1], 4-nonylphenol (4-NP)[1], 4-chloro-3-methylphenol (4-C-3-MP)[1], 4-octylphenol (4-OP)[1], 4-tert-octylphenol (4-t-OP)[1], 2-phenylphenol (2-PP)[1], bisphenol A (BPA)[1,2], bisphenol S (BPS)[2], bisphenol E (BPE)[2], bisphenol B (BPB)[2], 4-cumylphenol (HPP)[2], bisphenol F (BPF)[2]	GC-MS[1], HPLC-MS/MS[2]	Paper III[1] Paper IV[2]
	Phthalates	Bis (2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), di (2-methoxyethyl) phthalate (DMEP), didecyl phthalate (DDP), dicyclohexyl phthalate (DCHP), dibutyl phthalate (DBP), di-iso-butyl phthalate (DiBP), didecyl phthalate (DPP), diethyl phthalate (DEP), dimethyl phthalate (DMP)	GC-MS	Paper III
	Polychlorinated biphenyls	PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180	GC-MS	Paper III
	Toxic metals	Cd, Co, Cr, Cu, Ni, Pb	ICP-MS	Paper III
PLASTICS	Brominated flame retardants	Tetrabromobisphenol A (TBBPA), hexabromocyclododecane stereoisomers (α-, β-, and γ-HBCD), 2,4 - dibromophenol (2,4-DBP), 2,6-dibromophenol (2,6-DBP), 2,4,6-tribromophenol (2,4,6-TBP)	HPLC-MS/MS	Paper VI
	Phthalates	Bis (2-ethylhexyl)phthalate (DEHP), butyl benzyl phthalate (BBP), didecyl phthalate (DDP), dicyclohexyl phthalate (DCHP), dibutyl phthalate (DBP), di-iso-butyl phthalate (DiBP), didecyl phthalate (DPP), diethyl phthalate (DEP), dimethyl phthalate (DMP)	GC-MS	Paper V

*FID: flame ionization detector; GC: gas chromatograph; ICP: inductively coupled plasma; MS: mass spectrometer.

2.5 Material and substance flow modelling

Material flow analysis (MFA) is a tool based primarily on law of mass conservation and used to systematically quantify flows of materials in arbitrarily complex systems [53]. When MFA is focused on chemicals rather than materials containing them, it is commonly referred to as substance flow analysis (SFA) [54]. SFA is a sophisticated approach that can provide information on flows, distribution and losses of chemicals in product and material cycles. MFA describing a system at a specific time is called static,

contrary to a dynamic MFA which describes flows and stocks of materials over time [55]. A combination of static and dynamic MFA can provide a comprehensive understanding of circular systems on the level of goods (materials) and substances (chemicals).

Combination of static and dynamic MFA was used to evaluate presence of selected chemicals (bisphenol A (BPA), DEHP, and mineral oil hydrocarbons (MOHs)) in the European paper cycle. STAN software, a widely used MFA tool, was used in static MFA modelling, offering possibility for data reconciliation and error propagation [56]. The approach used in this work consisted of four steps which are schematically represented in Figure 2-5 and described in details in Paper VII. In brief, in the **first step** the flows of paper in Europe were quantified, deriving a fully balanced system for the year 2012. The system reconciliation resulted in transfer coefficients describing the partitioning of paper flows (i.e. distribution of inputs between the outputs) in each of the processes. These transfer coefficients and concentrations of BPA, DEHP, and MOHs in the waste paper (based on the data provided in Paper III and IV) were used to create SFA model of chemicals in the paper cycle in the **second step**. Based on the outputs from step one and two, a dynamic model on material (goods) and substance (chemical) levels was developed in **step three**. Finally, in the **last step**, a set of scenarios was used to evaluate the effects of potential mitigation measures on presence of chemicals in the paper cycle. The four scenarios evaluated were defined as follows (see Paper VII for details):

i) Scenario zero (SC0). A reference scenario (no mitigation measures implemented).

ii) Scenario 1 (SC1). Designed to constrain accumulation and spreading of contamination. Source-segregation of waste paper was optimized, indicating which fractions should additionally be included or excluded form waste paper for recycling. Current paper recycling rates were used as a constraint.

iii) Scenario 2 (SC2). Evaluates removal of contaminants. The decontamination of paper in waste paper re-processing was assumed to be doubled within a year.

iv) Scenario 3 (SC3). Prevention of contamination. BPA, DEHP, or MOHs were assumed to be phased out (linear reduction) within a period of five years until no chemical was added in production of paper articles.

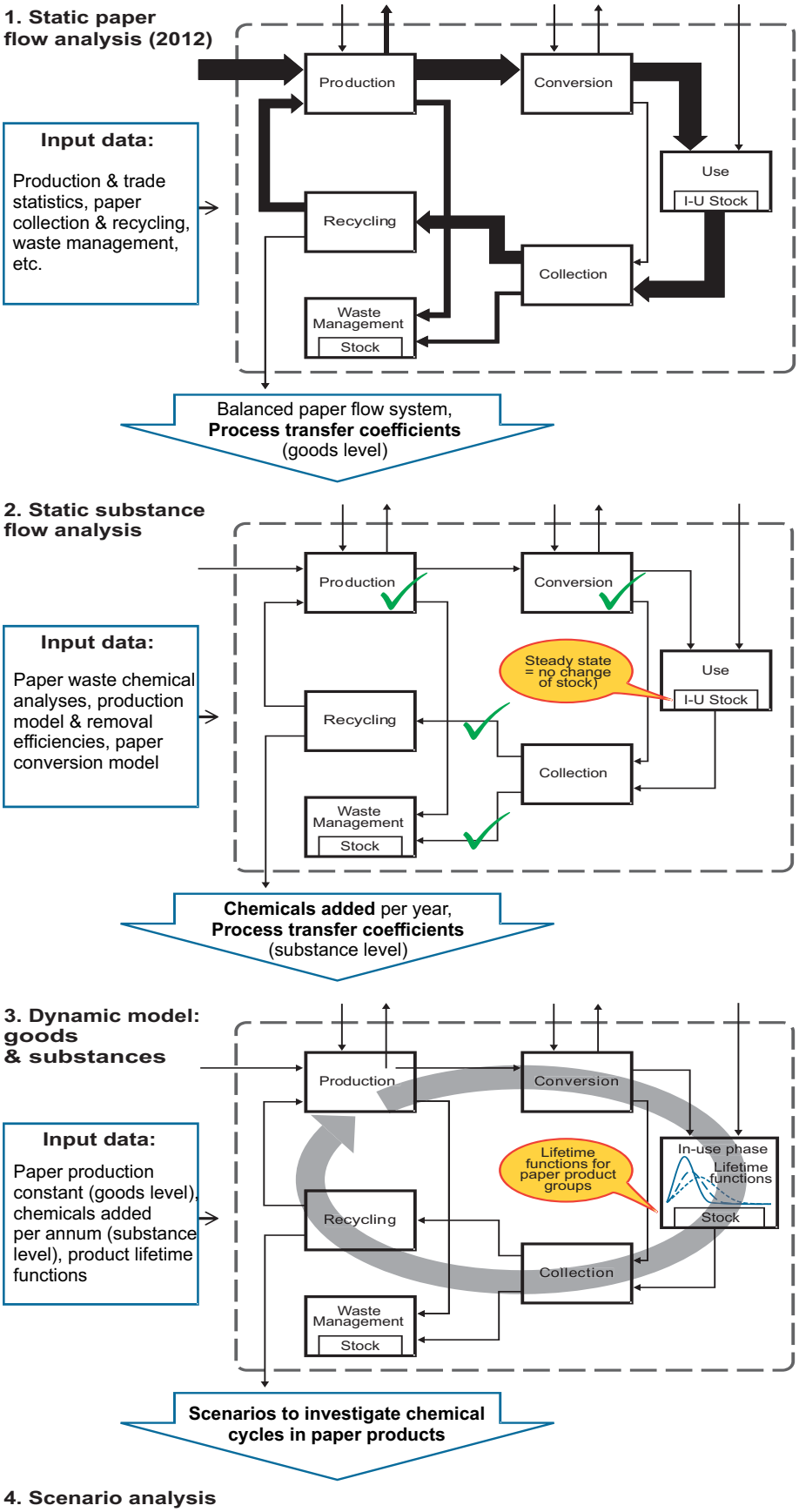


Figure 2-5 Schematic representation of the modelling approach (Paper VII).

3 Literature review

3.1 State-of-the-art in literature

Information on chemicals either intentionally used or being part of contamination and present in materials and products is sparse. Producers may not be obliged to disclose the lists of all the chemicals being directly or intermittingly used in the manufacturing process. Moreover, NIAS would still not be part of such lists, as their identity is not always known and producers may not always be aware of their presence in materials [7]. Hence, an illustrative attempt was made to document the chemicals potentially present in a material on the example of paper and paper products. As Table 2-1 indicates, almost 10,000 could potentially be present in paper and paper products. The vast majority of the chemicals were associated with printing industry, where approx. 4600 and approx. 3900 can be used in the manufacture of packaging and food packaging inks, respectively. These chemicals are used as solvents, dyes, pigments, binders, plasticisers, surfactants, etc. Although used in large volumes [57], number of chemicals associated exclusively with production of paper as a material was minor (66). These chemicals are used as fillers, binders, retention aids, coaters, biocides, etc.

3.2 Hazard identification

Following the procedure presented in Figure 2-4, chemicals with hazard potential among the ones outlined in Table 2-1 were identified. Due to the nature of approach, only chemicals that could be assigned a valid CAS number were taken into account. This could potentially result in underestimation of the number of hazardous chemicals identified in this work. For example, chemicals resulted from analytical literature were approx. 1400, but only 348 were selected (Table 2-1) once CAS numbers were assigned and duplicates were removed.

Applying the defined criteria, among the approx. 10,000 chemicals initially selected 157 chemicals were identified as hazardous and potentially problematic for paper recycling. Among those chemicals, following groups were identified: mineral oils, phthalates, phenols, parabens, etc. Most of the chemicals were attributed to the printing industry and were part of solvents and polymeric resins employed in inks, pigments, and dyes. Detailed distribution of use of the selected chemicals is provided in Figure 3-1 (a). Paper production

was responsible for 10 chemicals, which were predominantly biocides used in bacteria-favouring conditions occurring in the production of paper.

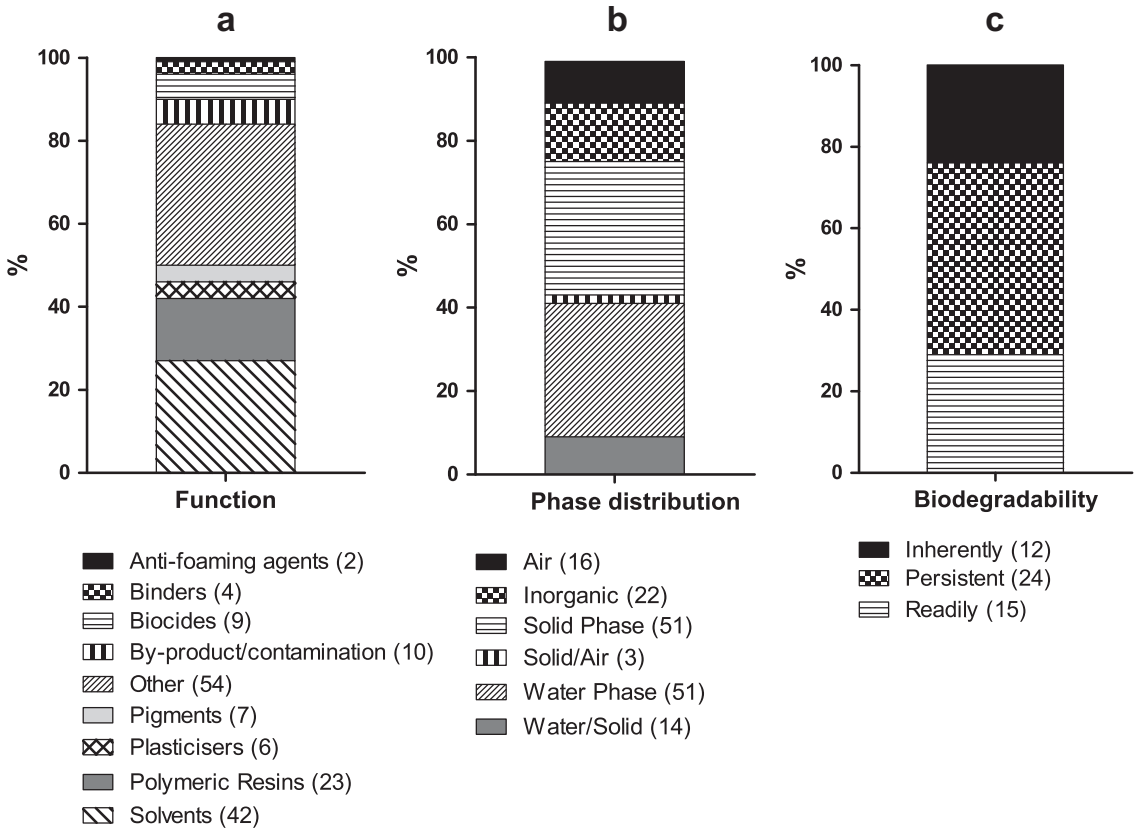


Figure 3-1 Distribution of the use of the potentially hazardous chemicals associated with paper and paper products (a); phase distribution of the potentially hazardous chemicals associated with paper and paper products (b); biodegradability of chemicals associated with the solid phase as identified in the phase distribution (c) (Paper II).

As illustrated in Figure 3-1 (b), most of the hazardous chemical identified would show affinity either to solid phase (and be potentially adhered to paper fibres in re-processing) or water phase (and be potentially removed in paper re-processing). Such approach in assessing phase distribution of a chemical is a simplification, as the actual distribution of a chemical in paper re-processing will depend on a number of factors (e.g., type and number of steps in paper re-processing, temperature, pH, residence time, type and amount of chemicals used in re-processing, etc.) and should be determined on a case-by-case basis. Of the total of 51 chemicals showing affinity to the solid phase, a rather small fraction (5) could not be attributed to any sectors within the paper industry. These chemicals could potentially represent examples of NIAS, i.e. chemical by-products or contaminants introduced into the production cycle through recycled paper.

Among the chemicals associated with solid phase in Figure 3-1 (b), the majority (24 out of 51) were resistant to biodegradation and were classified as persistent. These chemicals would require additional attention related to their presence in recycled materials and potential release in paper re-processing.

Although the overview of chemicals potentially present in paper was not intended to be exhaustive, it nevertheless indicated that concerns about presence of chemicals in materials can be restricted to relatively small number of potentially problematic chemicals. The work provided a systematic basis for identification of chemical contaminants potentially detrimental to material recycling. Furthermore, it also demonstrated a need for more comprehensive quantitative data documenting levels of chemical contamination of paper products and by extension waste paper recovered for recycling.

4 Chemicals in recyclables

4.1 Fractional composition of waste materials

Sampled waste paper and plastics were sorted into detailed fractions. Waste paper and board were sorted into the total of 30 fractions. The relative composition of paper and board in the residual and source-segregated waste material flows is provided in Table 4-1. Differences between the two flows reflect the waste sorting and segregation guidelines applied in the municipality where samples were obtained from (Paper III). The majority (72 %) of waste paper and board came from advertisements, newspapers and magazines. Higher share of board in the residual waste (approx. 43 % compared to approx. 13 % in the source-segregated waste) was the result of larger waste board items being collected at recycling stations (rather than disposed in source-segregated waste), while smaller board items being either contaminated in use (e.g., used pizza boxes as an example of food packaging) or not being currently recycled (e.g., beverage cartons).

Fractional composition of the collected waste plastics is presented in Table 4-2. The distribution of plastics between residual and source-segregated waste flows was similar (56 % and 44 %. respectively), potentially due to rather recently established waste plastics collection scheme. The polymers being source-segregated are primarily PET and HDPE (approx. 70 %) and to a lower extent PP (approx. 13 %). On the other hand, most of the plastics in the residual waste flow (approx. 40 %) were non-specified and can represent a mixture of polymers commonly found in households. PP was the second largest fraction in the residual waste flow. While composition of the total waste plastics collected correlated well with the European plastics demand [14] for some polymer types (e.g., HDPE and PP), other polymer types (e.g., PET, PVC and LDPE) do not usually end up in household waste due to alternative collection schemes established. For example, PET is predominantly used in beverage bottles that are part of a deposit-and-return system, assuring closed-loop recycling of plastic bottles.

Table 4-1 Composition of residual and source-segregated waste paper and board (% wet weight). Residual and source-segregated flows contributed with 21 % and 79 % of the total sample collected, respectively (Paper III).

	#	Fractions	Residual [%]	Source-segregated [%]	Total [%]
Paper	F1	Advertisements (non-glued)	7.9	28.1	23.8
	F2	Advertisements (glued)	4.4	20.1	16.8
	F3	Newsprint advertisements (non-glued)	2.7	5.0	4.5
	F4	Newsprint advertisements (glued)	1.6	3.0	2.7
	F5	Newspapers	9.8	17.2	15.6
	F6	Magazines, Journals, TV guides (non-glued)	3.8	6.5	6.0
	F7	Magazines, Journals, TV guides (glued)	1.5	3.0	2.7
	F8	Office and administrative paper	12.9	3.0	5.1
	F9	Envelopes	2.5	0.4	0.9
	F10	Wrapping paper	0.9	0.1	0.3
	F11	Receipts	0.7	<0.1	0.1
	F12	Self adhesives	0.1	<0.1	<0.1
	F13	Books and booklets	2.0	0.7	1.0
	F14	Phonebooks	0.4	0.0	0.1
	F15	Tissue paper	0.9	<0.1	0.2
	F16	Kraft paper (brown and bleached)	2.1	0.2	0.6
	F17	Other paper[1]	2.2	0.1	0.5
		Total paper (F1-F17)	56.6	87.3	80.8
Board	F18	Corrugated boxes - shipping	1.7	1.2	1.3
	F19	Corrugated boxes - sales (Food packaging)	4.1	4.1	4.1
	F20	Corrugated boxes - sales (Non-food packaging)	0.8	2.9	2.5
	F21	Folding boxes - shipping	0.0	0.0	0.0
	F22	Folding boxes - sales (Food packaging)	8.9	2.0	3.5
	F23	Folding boxes - sales (Non-food packaging)	5.7	0.9	1.9
	F24	Egg trays and alike	1.2	0.3	0.5
	F25	Tubes	4.5	0.2	1.1
	F26	Beverage cartons	11.9	0.2	2.7
	F27	Paper plates and cups	0.5	<0.1	0.1
	F28	Composites[2]	0.5	0.1	0.2
	F29	Cards and labels	1.7	0.3	0.6
	F30	Other cardboard[1]	1.9	0.3	0.6
		Total board (F18-F30)	43.4	12.7	19.2
		Total (F1-F30)	100	100	100

[1] Includes articles of paper and board not covered by the fractions F1-F16 for paper, and F18-F29 for board (e.g., greaseproof and baking paper); [2] Includes predominantly articles of board laminated with aluminum or plastics and not included in the remaining board fractions (e.g., Pringles® potato-based snack packaging).

Table 4-2 Composition of residual and source-segregated waste plastics (% wet weight). Residual and source-segregated flows contributed with 56 % and 44 % of the total sample collected, respectively (partially based on data from Paper I).

#	Fractions	Residual [%]	Source-segregated [%]	Total [%]	European plastics demand [14]
F1	PET	17.4	30.3	23.1	6.9
F2	HDPE	13.5	37.9	24.3	12.1
F3	PVC	0.1	<0.1	0.1	10.4
F4	LDPE	0.2	0.4	0.2	17.5
F5	PP	24.8	12.9	19.5	18.9
F6	PS	5.4	2.1	3.9	7.1
F7	PS foamed	0.3	<0.1	0.2	
F8	ABS	<0.1	1.1	0.5	27.1
F9	Non-specified	38.3	15.3	28.1	
	Total	100	100	100	100

4.2 Quantification of chemicals in paper and plastics

Selected chemicals, potentially being problematic for assuring quality paper and plastics recycling, were quantified in the collected samples. The results of the analyses are provided in the following sections with respect to paper (section 4.2.1) and plastics (section 4.2.2). All the presented and discussed concentrations refer to the dry matter (dm) content of the respective material.

4.2.1 Paper

Figure 4-1 provides the concentration ranges (min-max) of the selected chemicals analysed in the samples of residual and source segregated waste paper (Paper III, Supporting Information). The values presented are in logarithmic scale. It is evident from the figure that concentrations differed considerably from one group of chemicals to another. As an example, mineral oils ranged between approx. 100 and approx. 10,000 mg/kg, while concentrations of polychlorinated biphenyls (PCBs) were between approx. 0.0001 and approx. 0.01 mg/kg. Furthermore, not all constituents of a chemical group were quantified in similar concentrations. For example, the highest concentrations measured for DDP and BBP (both phthalates) were 0.22 and 330 mg/kg, respectively. While presence of some of the contaminants due to natural wood constituents could not be eliminated (e.g., selected toxic metals), majority of the analysed chemicals are not expected to occur due to natural constituents of primary raw materials used in paper making (Paper III).

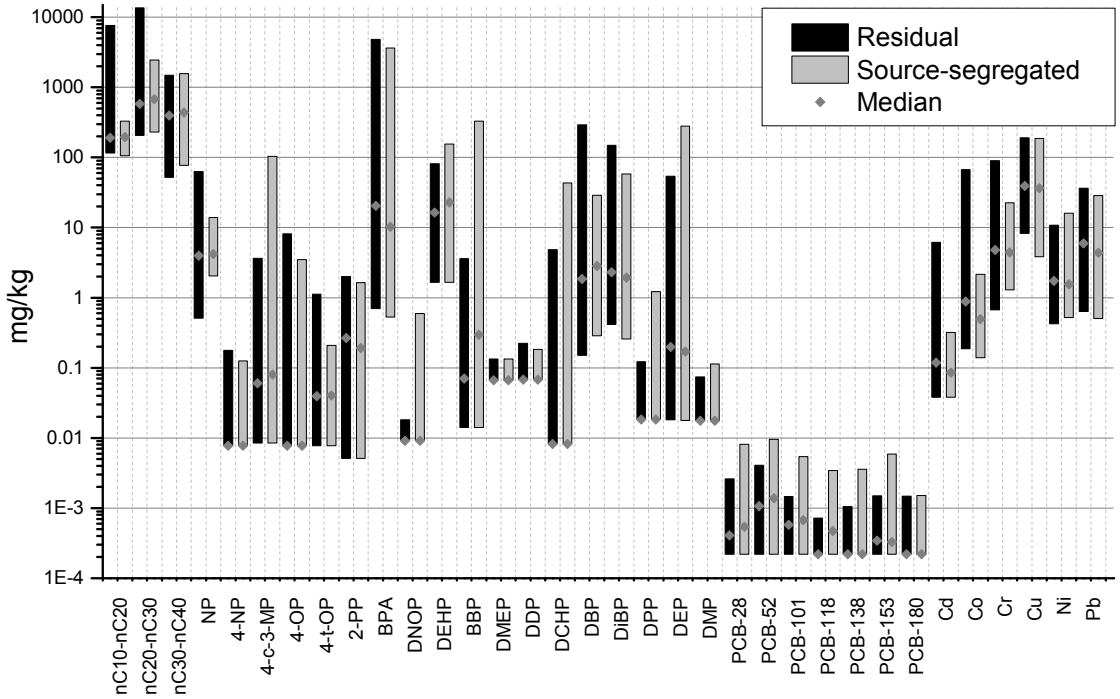


Figure 4-1 Concentration ranges (min-max) and median concentrations of chemicals in residual and source-segregated waste paper; logarithmic scale in mg/kg dm (Paper III).

In the manual sorting of waste paper and board a distinction between glued and non-glued articles (e.g., advertisements and newsprints), as well as food and non-food packaging (e.g., corrugated and folding boxes) was made (see Table 4-1 for details) in order to evaluate whether such a distinction would influence the hazardous chemicals content. Unfortunately, no clear trends were observed. An exception was the total phthalate content, where non-food packaging board revealed higher concentrations when compared to food packaging board, suggesting limited use of phthalates or presence of recycled fiber in food packaging board (Paper III).

Comparing the results for residual and source-segregated waste paper, only phthalates and PCBs showed no significant difference. Median concentrations of the remaining groups of chemicals (i.e. mineral oils, phenols and toxic metals) were higher in residual waste paper. This potentially indicates that cross-contamination during residual waste paper collection, as well as the potential differences in the use and disposal patterns of the individual paper and board items in the two waste flows, have a significant influence on the total content of mineral oils, phenols and toxic metals in the waste paper.

Being banned for decades in most of the world (1977 and 1984 for USA and Europe, respectively [58]), makes rather surprising the presence of PCBs in the samples of waste paper analysed. Historically PCBs were used in the ink capsules of carbonless copy paper, which would burst and release PCBs in waste paper re-processing contaminating the newly manufactured paper products [59]. Thus, paper articles based on recycled paper and produced mainly between 1970s and 1980s had relatively high (up to 12.4 mg/kg) PCB content [60]. Providing such paper articles have long lifespan and are being recycled nowadays would result in promoting re-introduction of PCBs in the paper loop. Affirmatively, the highest concentration of ∑PCBs we measured (0.32 mg/kg) was in the waste paper fraction containing paper products with long lifespan (e.g., books and archives). Rather high concentrations of ∑PCBs measured in selected board fractions (e.g., up to 0.12 mg/kg in corrugated boxes), expected to contain a substantial share of recycled fiber, could indicate relatively slow process of PCB contamination removal from the paper loop.

It is evident from Figure 4-1 that the maximum concentrations of the controversial chemical BPA [61] were among the highest for contaminants measured in waste paper and comparable to those of mineral oils. This was the result of thermal paper use in the receipts found in waste paper. A detailed study focused on BPA and its analogues (Paper IV), showed that thermal paper receipts is the main source of BPA in waste paper. The median concentrations measured in the thermal paper receipts (16,300 mg/kg) were substantially higher than the remaining paper and waste paper fractions analysed (Table 4-3). Lower concentrations of BPA in waste receipts (8100 mg/kg) when compared to the receipts obtained directly from retailers is due to the potential presence of BPA-free and non-thermal paper receipts in the former. High concentrations of BPA measured in thermal paper receipts and its abundance in the analysed samples of waste paper indicated potential contamination through the paper recycling process, which is also supported by potentially low BPA removal (approx. 10%) in paper re-processing [62].

Public pressure to reduce or even eliminate use of BPA, resulted in gradual increase in use of BPA analogues in selected applications (including thermal paper). Evaluating the potential BPA analogues, indicated that bisphenol S (BPS) has clearly been the main alternative used for substitution of BPA in paper applications (Paper IV). It was measured in high concentrations (median of 7800 mg/kg) in thermal paper receipts not containing BPA and was quantified in most of the waste paper samples analysed. On the other hand, none of the remaining BPA alternatives evaluated (i.e. bisphenol E (BPE),

bisphenol B (BPB), 4-cumylphenol (HPP), and bisphenol F (BPF)) was quantified in thermal paper receipts, indicating their limited use as BPA substitutes.

Table 4-3 Median concentration of BPA and its structural analogues (mg/kg dm) in thermal paper, paper products (NCR: non-carbon copy paper), and residual waste paper (based on the data provided in Paper IV).

		BPA [80-05-7]	BPS [80-09-1]	BPE [2081-08-5]	BPB [77-40-7]	HPP [599-64-4]	BPF [620-92-8]
Paper	Receipts	16,300[1]	7800[1]	<4	<3	<6	<4
	NCR	35	<7	<4	<3	<6	<4
	Printer paper	<2	<7	<4	<3	<6	<4
Waste paper	Receipts	8100	170	<0.04	<0.03	<0.06	<0.04
	Corrugated boxes	8.4	1.3	<0.04	<0.03	<0.06	0.080
	Newspapers	2.2	<0.07	<0.04	<0.03	<0.06	<0.04
	Flyers	2.8	0.22	<0.04	<0.03	<0.06	<0.04
	Office paper	280	0.54	<0.04	<0.03	<0.06	<0.04
	Envelopes	36	0.43	<0.04	<0.03	<0.06	<0.04
	Folding boxes	5.2	0.29	<0.04	<0.03	<0.06	0.043
	Magazines	0.80	<0.07	<0.04	<0.03	<0.06	<0.04
	Beverage cartons	0.41	<0.07	<0.04	<0.03	<0.06	<0.04
	Books	17	0.56	<0.04	<0.03	1.3	<0.04

[1] Lowest concentrations (<20 µg/g) were excluded from median value calculations.

4.2.2 Plastics

Similarly to the case of paper (see section 3.2 for details), chemicals of potential concern are also present in plastics. Recent report has outlined 43 chemicals potentially used in plastics and considered hazardous [63]. Contrarily to the procedure for literature review and hazard identification applied on paper (section 2.2), the report did not explicitly include analytical literature omitting in this way NIAS potentially present in plastic products, waste plastics and recycled plastics. Thus, the list of chemicals actually present in plastics can potentially be longer. Nevertheless, among the chemicals identified in the report main groups of chemicals included phthalates, toxic metals, brominated flame retardants (BFRs), polyaromatic hydrocarbons (PAHs), etc.

Phthalates are mostly used as plasticizers in plastic production, with largest share of the plasticizers market being attributed to polyvinyl chloride (PVC)

production [64]. Depending on their carbon chain length, phthalates are commonly divided into low and high molecular weight (i.e. LMW and HMW, respectively). LMW phthalates are prone to migration, making them more relevant for human toxicity. This has also resulted in restrictions on their use in selected applications in plastic materials (e.g., food-contact articles and children's toys) [65,66]. Nevertheless, in-depth toxicological profile of phthalates and potential further restrictions on their use is an area of active research [67,68]. Based on the quantitative analytical results of this work, di-iso-butyl phthalate (DiBP), DEHP and DBP are LMW phthalates found in the majority of plastics (Paper V). As Figure 4-2 indicates, DEHP was the dominant phthalate found in relatively high concentrations (up to 2700 mg/kg) in the majority of the plastic samples analysed. Furthermore, it was shown that between resin type and source of plastic samples, only latter had a significant influence on plastic phthalate content (Paper V).

Among the evaluated sources of plastics (see Figure 4-2 caption for details), virgin and recycled industrial plastics (group 1) were shown to have similar phthalates content. Furthermore, residual and source-segregated waste plastics and recycled household plastics (group 2) were also similar as to their phthalate content. On the other hand, group 1 and group 2 were significantly different, with group 2 having higher phthalate content. Based on the systematic statistical assessment of results for the evaluated samples, this could indicate that phthalates are added in later stages of plastic product manufacturing (labelling, gluing, etc.) and are not removed in the re-processing of plastics, making recycling a potential source of phthalates in products based on recycled waste material. Among the LMW phthalates analysed, one specific phthalate (DEHP) was abundant in plastics and played an important role in the differences between plastic sample sources (e.g., waste plastics and virgin plastics). Hence, DEHP can potentially be used as an indicator phthalate when recycled plastics are used in phthalate-sensitive applications (e.g., plastic food packaging).

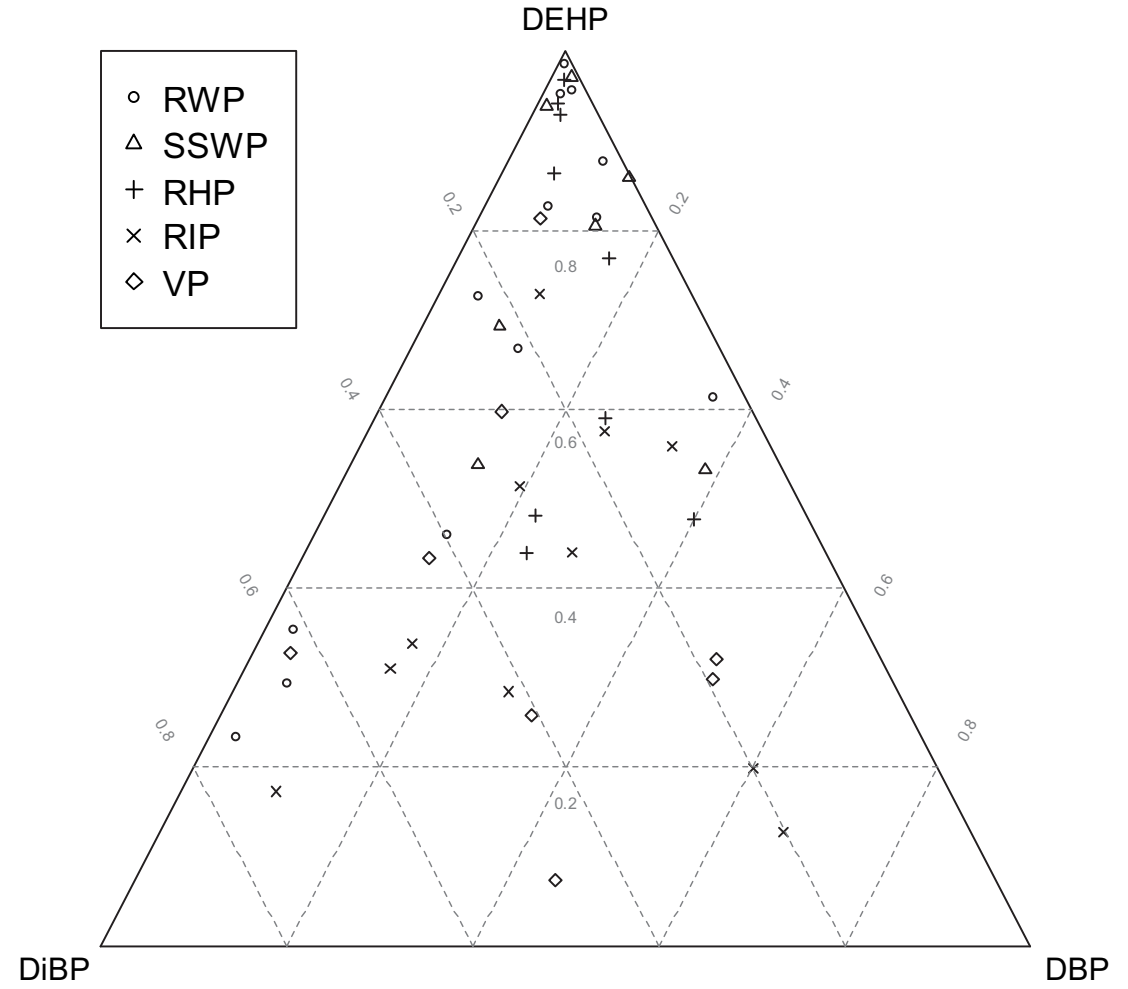


Figure 4-2 Ternary plot of plastic composition with respect to DiBP, DEHP and DBP. RWP Residual Waste Plastics; SSWP Source-Segregated Waste Plastics; RHP Recycled Household Plastics; RIP Recycled Industrial Plastics; VP Virgin Plastics (Paper V).

Flame retardants is another group of chemicals identified to be an important contaminant in plastics [63,69]. Flame retardants are used to decrease the potential risks of fires and, in case of plastics, are predominantly used in electric and electronic equipment, where wiring boards, electrical connectors, enclosures and cables are exposed to elevated temperatures and potential sources of ignition. Flame retardants are commonly divided into four groups in accordance to the main chemical constituent used, i.e. halogenated organic, phosphorus-containing, nitrogen-containing and inorganic [4]. The largest market share is attributed to a subgroup of halogenated organic - brominated flame retardants (BFRs). The subgroup contains well-established BFRs produced in large volumes, i.e. hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA), as well as emerging phenol-based BFRs (e.g., 2,4-dibromophenol (2,4-DBP) and 2,4,6-tribromophenol (2,4,6-TBP)).

The abundance of articles containing flame retardants and their persistent nature resulted in their accumulation in the environment in general and humans in particular [70,71]. Although potential effects of flame retardants will depend on the specific group (or a constituent) in focus, health and environmental issues associated with selected BFRs have been recognized and resulted in their classification as substances of very high concern (SVHC) and inclusion on the list of chemicals covered by the Stockholm Convention on Persistent Organic Pollutants (POPs). In turn, this resulted either in complete ban or restrictions on their use [72,73].

Polystyrene (PS) is a polymer commonly used in packaging, construction sector (e.g., insulation) and electric and electronic equipment [14]. It has also been shown to contain the highest concentrations of ∑HBCD (up to 1,100,000 ng/g) and TBBPA (up to 13,000 ng/g), followed by the non-specified plastics ("other") and polypropylene (PP) (Figure 4-3). HBCD was subjected to authorization in the EU from August 2015 under the REACH regulation [20], but was present in the plastic samples we analysed (collected in 2013). Use of PS in construction sector (usually associated with comparatively long lifespan applications) points out the issue with "legacy" contamination of plastic material, similarly to presence of PCBs in paper (see section 4.1.1 for details). While HDPE contained among the lowest concentrations of ∑HBCD and TBBPA, packaging waste HDPE (both source-segregated and residual) also contained the highest concentrations of 2,4-DBP and 2,6-dibromophenol (2,6-DBP) (Figure 4-4). Presence of 2,4-DBP and 2,6-DBP was quantified predominantly in waste plastics rather than in samples of processed plastics. In addition to the direct use of selected BFRs, relatively high concentrations of 2,4-DBP (240 ng/g), 2,6-DBP (250 ng/g) and TBBPA (7000 ng/g) in a sample of processed plastics, could be attributed to thermal degradation of TBBPA and production of dibromophenols as by-products.

Finally, the plastic recycling process may also influence the transformation of contaminants contained in the waste material being recycled. As an example, among the three isomers of HBCD measured, α-HBCD was found in relatively higher concentrations compared to β- or γ-HBCD (Paper VI). This contradicted the common composition of commercial HBCD mixtures, where γ-HBCD is the dominant isomer [74]. Since exposing HBCD to temperatures > 100ºC promotes the transformation of γ-HBCD to α-HBCD [75], temperatures commonly applied in thermoplastics re-processing (135-245^{o}C [76]) can alter the diastereometric ratio of a HBCD mixture and explain the prevalence of the α-HBCD in all the samples of recycled plastics analysed (Paper VI).

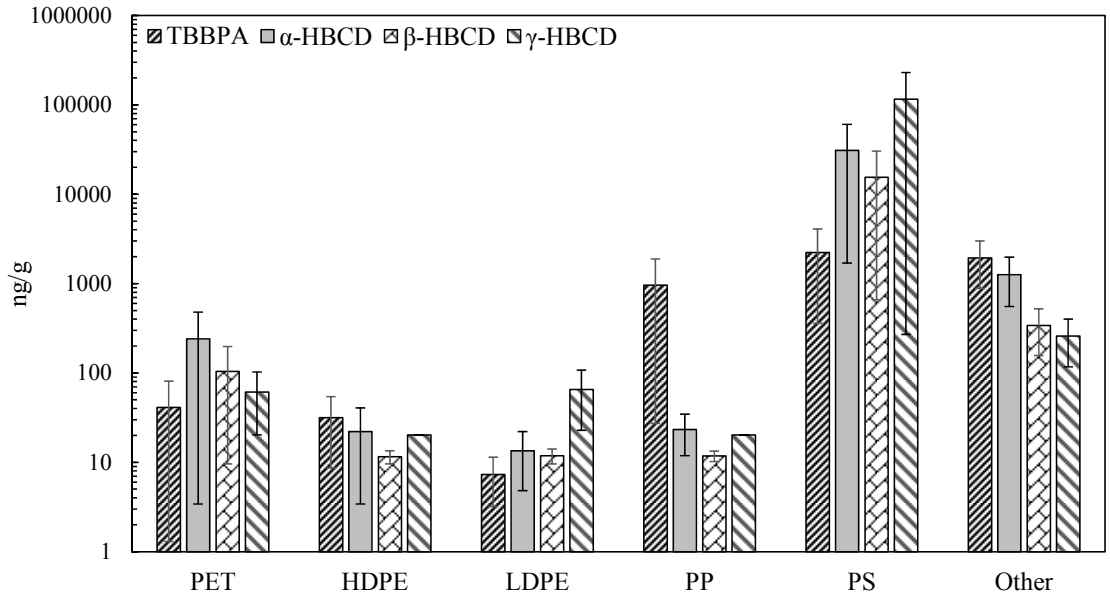


Figure 4-3 Concentrations of TBBPA and HBCD isomers (logarithmic scale) in plastics by resin. Bars indicate the average concentrations across the samples analysed (i.e. virgin, waste, and recycled plastics) while error bars show standard error in the aggregated values (Paper VI).

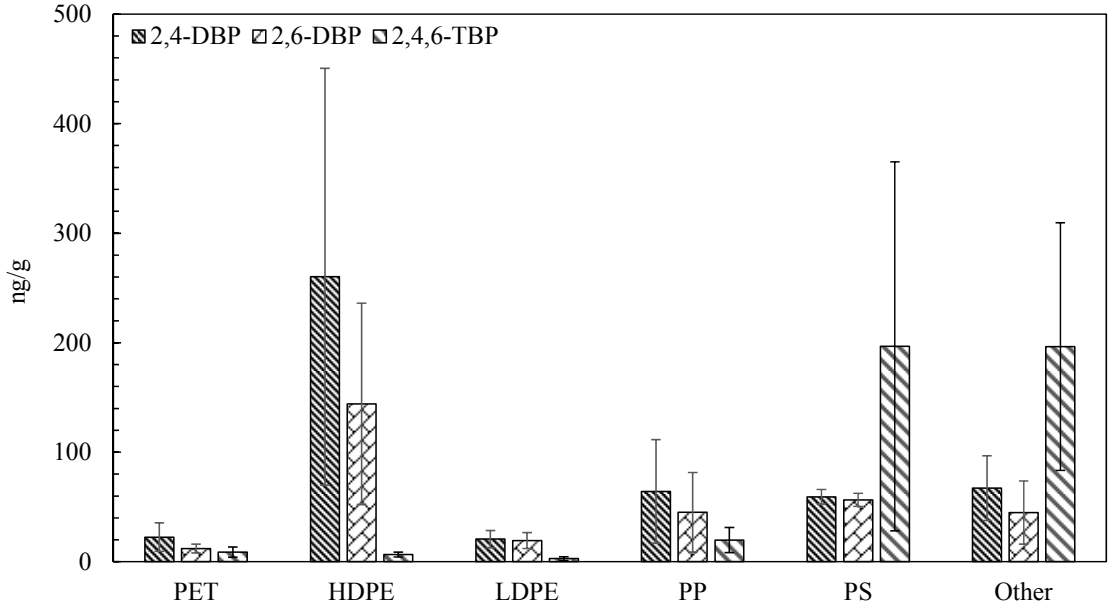


Figure 4-4 Concentrations of 2,4-DBP, 2,6-DBP, and 2,4,6-TBP in plastics by resin. Bars indicate the average concentrations across the samples analysed (i.e. virgin, waste, and recycled plastics) while error bars show standard error in the aggregated values (Paper VI).

5 Material cycles

5.1 Chemical contaminants in material cycles

Chemicals can be introduced into materials from a variety of sources in different processes. Following the example of paper (Figure 5-1), chemicals are introduced: i) in the paper production itself, either directly added or being part of NIAS; ii) in paper conversion as part of printing inks and adhesives, paper imports and NIAS; iii) in paper consumption, as part of paper product imports or NIAS; iv) in waste collection as NIAS; and finally v) as part of waste paper imports in paper collected for recycling.

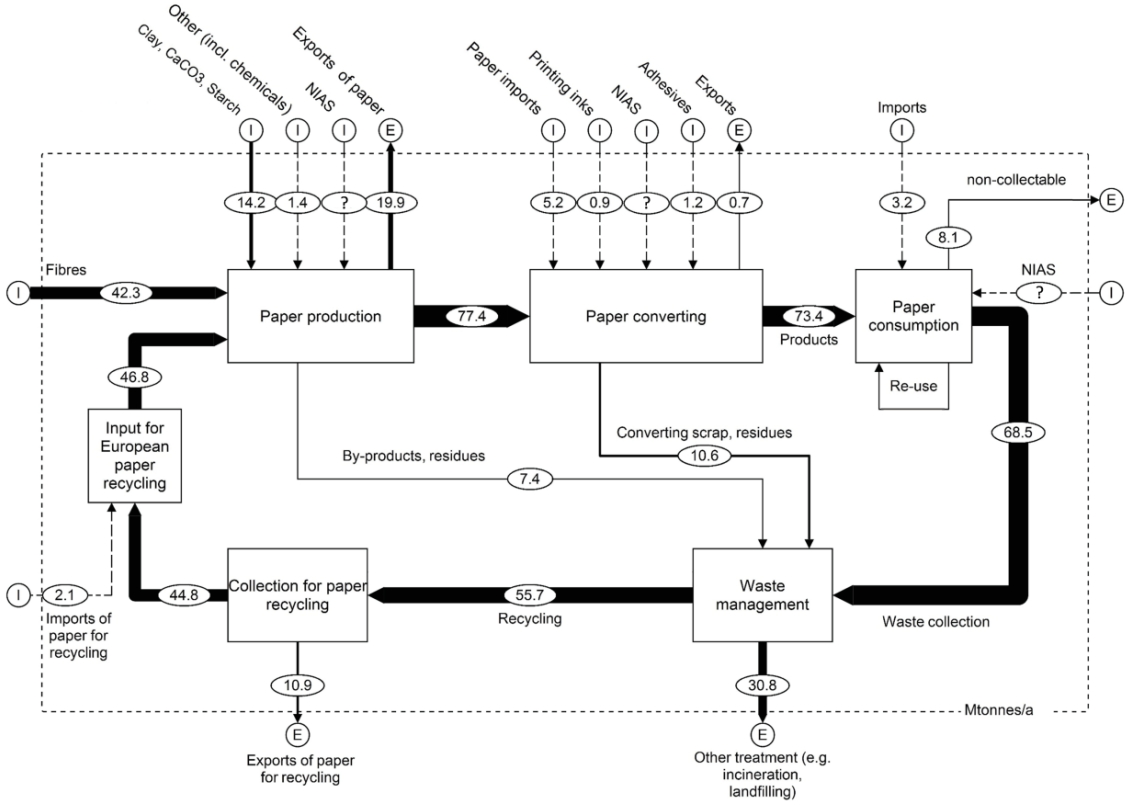


Figure 5-1 Material flow of the European paper recycling loop. Dotted lines indicate points where chemicals are potentially introduced (Paper II).

In a given material cycle, chemicals are constantly added and removed from the loop. In case the rate of removing chemicals (i.e. decontamination) is lower than the rate of their addition, accumulation of chemical contaminants in the newly manufactured products can be expected. Such accumulation trends were illustrated on the example of BPA, DEHP, and MOHs in the European paper products (Figure 5-2). Initial system was assumed free of contamination and chemicals were added at constant rates starting at year zero. High initial

amounts of BPA presented in Figure 5-2 resulted from addition of BPA in (thermal) paper production, while both DEHP and MOHs were assumed to be used only in paper conversion (i.e. printing). Recycling of paper and incomplete contaminant removal resulted in increasing amounts of chemicals in paper products over time, up until an equilibrium between addition and removal of a chemical to/from the material loop is achieved – marking steady state conditions.

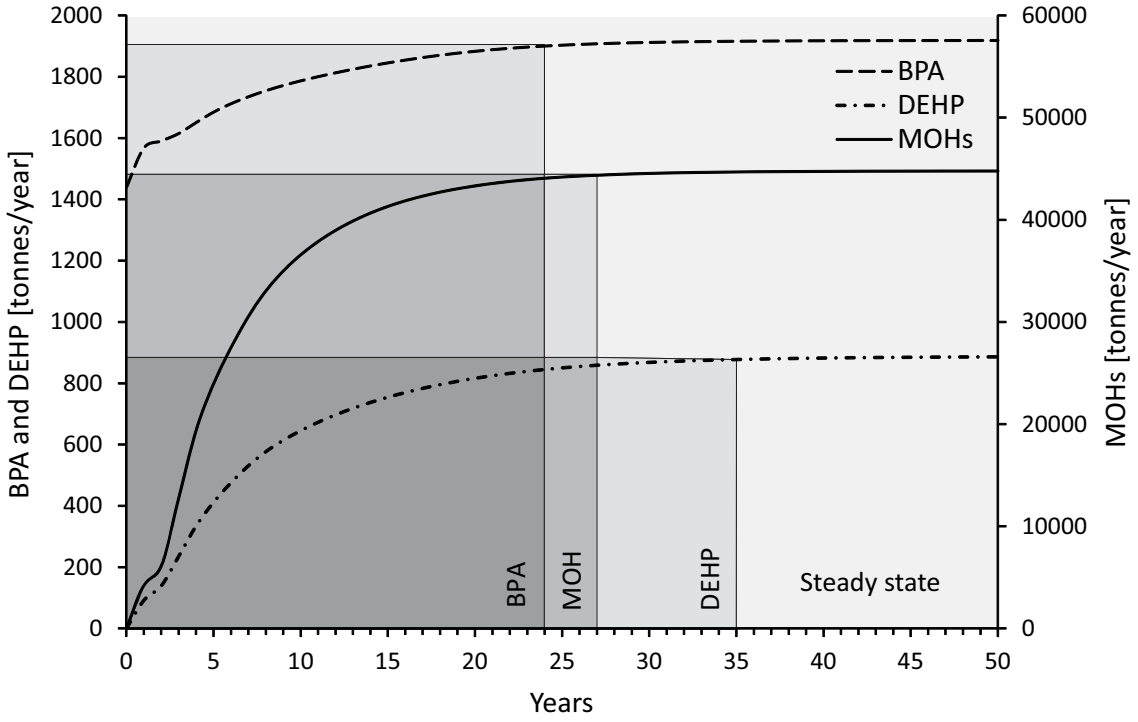


Figure 5-2 Evolution of chemical flows (BPA, DEHP, and MOHs) in paper products in the European paper loop (i.e. reference scenario, SC0). The shaded areas represent periods of accumulation for BPA, DEHP and MOHs, as well as the (quasi) steady state achieved (Paper VII).

Once the steady state is achieved, the total stocks of paper and chemicals in use can be calculated. As Figure 5-3 illustrates, fractional composition of paper in use stock is not equally distributed, i.e. the majority of paper is accumulated as other graphic paper, case materials and other paper. This was followed by carton board, while presence of the remaining fractions (e.g., newsprint) can be considered insignificant. This distribution reflects the lifespan function of paper products within each of the fractions, i.e. the shorter is a product's lifespan the lower will be its presence in the paper stocks (Paper VII). Furthermore, selected paper product categories differ as to their contaminant content, which also results in differences in chemical stocks in the product use phase. For example, approx. 80 % of BPA in stock is part of the other paper

fraction where thermal paper receipts are an important source of the contaminant. Similarly, case materials fraction contained the largest share (approx. 40 %) of MOHs. Finally, expressing the total stocks (as presented in Figure 5-3) per capita would result in 440 kg of paper, 30 g of BPA, 10 g of DEHP and 740 g of MOHs accumulated as stock per capita in Europe.

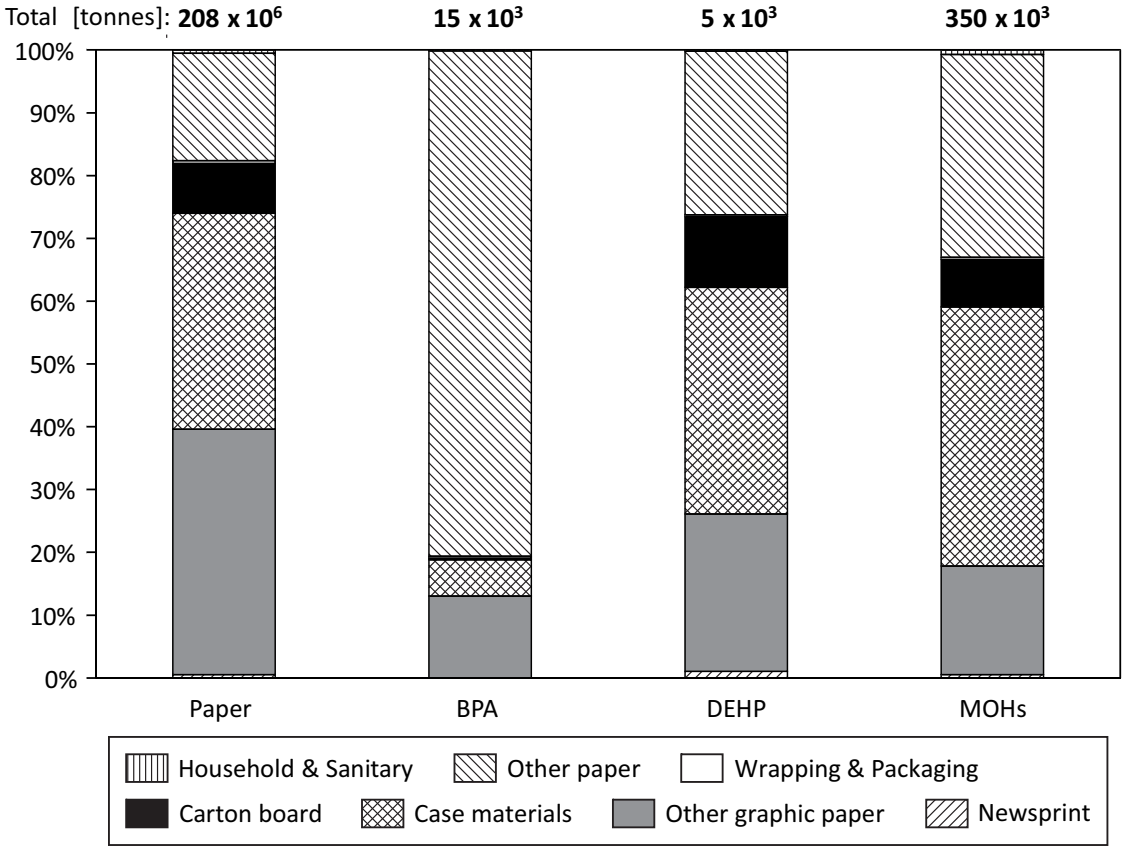


Figure 5-3 Total in-use stock of paper, BPA, DEHP and MOHs in the various paper product groups after a steady state was reached (Paper VII).

5.2 Mitigation of material contamination

In order to prevent or reduce the chemical contamination of material cycles, several approaches can be employed (Figure 5-4). The conceptual hierarchy of contaminant mitigation measures presented in Figure 5-4 is inspired by the waste management hierarchy (i.e., prevention, preparation for re-use, recycling, recovery, and disposal) outlined in the waste framework directive [77]. Intuitively, the prevailing approach would be to avoid contamination at the source and prevent the use (through phase out with or without substitution) of a specific chemical that can cause contamination. Nevertheless, some chemicals may not be phased out and the next mitigation measure would be to limit their use to specific application(s), thus constraining the potential

spreading of chemicals through e.g., positive or negative waste material selection. The next best alternative would be to remove a contaminant from the associated material through establishment or improvement of a decontamination technology in material re-processing (e.g., de-inking in paper recycling). These measures are focused on the contaminant, while the next two affect the material as well. If sufficiently efficient technology for material decontamination cannot be established, destruction of contaminated waste material (e.g., incineration) would take place. Finally, the materials that cannot be destroyed (due to e.g., legislative, technological or economic constraints) will be contained in a final sink (e.g., landfill).

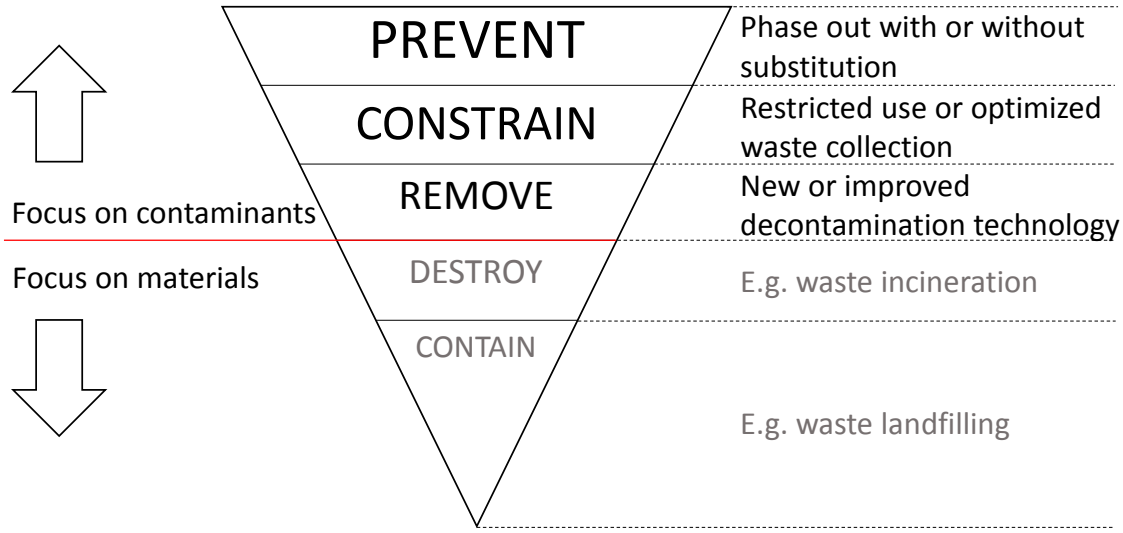


Figure 5-4 Qualitative hierarchy of measures for contaminant mitigation in material cycles.

The effects of contaminant-oriented measures (i.e., prevent, constrain and remove) on contaminant mitigation on the example of the European paper cycle and BPA, DEHP and MOHs as contaminants in focus are provided as results of the scenario evaluation in the following chapters (5.2.1 – 5.2.3). Each of the scenarios was compared to a reference scenario (SC0) where no mitigation measures were assumed (see section 2.5 for details).

5.2.1 Prevent (Phase out of chemicals)

Prevention or phase out of a chemical can result from developments in legislation or industry standards and obligatory or even voluntary discontinuation of its manufacturing or use. Usually, a discontinued chemical would be substituted with an alternative, although adjustments in production process may also avoid use of an alternative [78]. As an example, BPA in

thermal paper receipts has been gradually substituted by BPS, while other alternatives are also available on the market (Paper IV).

Measuring the effectiveness of prevention of chemical use suggested that placing it on the top of the intuitive hierarchy (Figure 5-4) is indeed reflected in its efficiency. As evident from the SC3 in Figure 5-5, preventing use of a chemical on the example of BPA, DEHP, and MOHs would results in its complete elimination (i.e. presence in material in concentrations lower than LOD) from paper material cycle. However, this could also require substantial time, as the removal rate of contaminants may be low. For example, it would take up to 26 years from the point in time where no BPA is added to paper material until the concentration of BPA in paper products can be considered insignificant (i.e. BPA stock depletion). This may create an issue of "legacy" contaminants, which was also pointed out by the analytical results of PCBs and HBCDs in paper (section 4.1.1) and plastics (section 4.1.2), respectively.

Although prevention has been shown to be the most efficient measure in contaminant mitigation, phasing out one chemical through substitution with another may result in "problem shifting". Following the example of BPA, one of the potential alternatives identified for its substitution (4-cumylphenol (Paper IV)) exhibited 12 time higher estrogenic activity comparing to BPA [79]. Hence, the mechanism of phasing out a chemical from a specific application or industry should be closely monitored to avoid potential trade-offs in the potential effects.

5.2.2 Constrain (Optimized waste collection)

Restriction on spreading contamination in material and product categories within a material cycle can be the result of legislation development (e.g., ban on use of BPA in baby and infant polycarbonate products (Paper IV)) or by maintaining closed loop recycling schemes where obsolete products are re-processed into products with similar applications or requirements (e.g., recycling of contaminated plastics from waste electric and electronic equipment (WEEE) into plastics used in electric and electronic equipment [80]). Alternatively, restriction of contamination can also be assured through optimization of waste material collection schemes, where contaminant-rich waste fractions are exempt from materials recovered for recycling. Such measures will be restricted by constraints imposed through ever-growing recycling rates, as selecting "clean" material streams gets more difficult the higher recycling rates are.

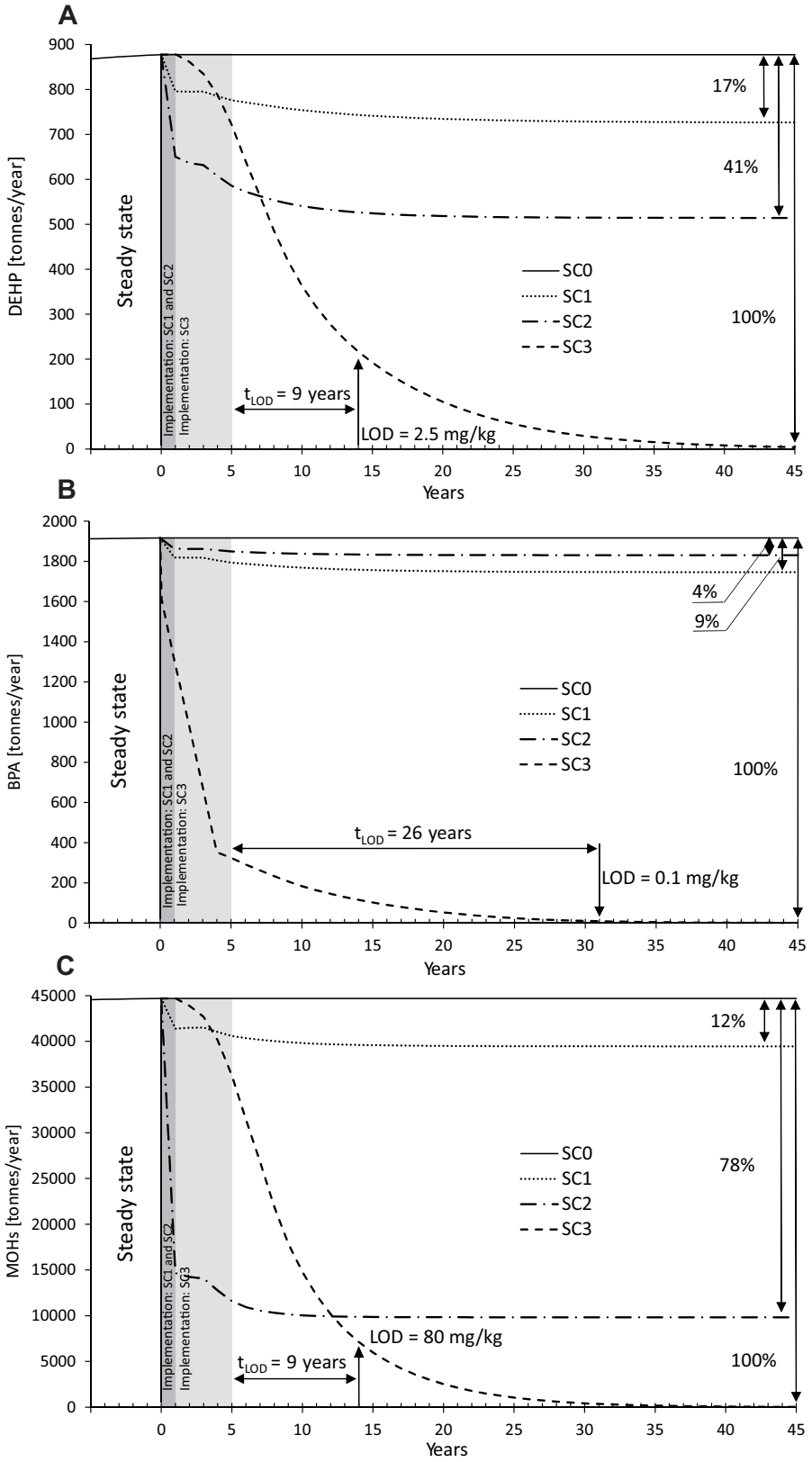


Figure 5-5 Evolution of DEHP (A), BPA (B) and MOHs (C) flows in paper products (output of paper production). Shaded areas represent implementation periods for SC1, SC2 and SC3. LOD: limit of detection; t_{LOD}: time required to achieve insignificant concentrations of respective chemicals (Paper VII).

As illustrated by SC1 in Figure 5-5, efficiency of optimized waste material collection has shown limited potential, as the highest reduction in contamination was 17 % for DEHP (Figure 5-5 (A)). Even lower values, 9 % and 12 % were achieved for BPA and MOHs, respectively. Main reason for such a low efficiency was the fact that recycling rates were constrained to the current levels (approx. 75 %). Hence, share of paper that could be diverted from recycling to e.g., incineration, as well as the respective share routed from residual to recovered paper, was limited. The importance of the recycling rate was shown when the recycling rates were lowered by 5 % (from approx. 75 % to 70 %). In such case, the potential reduction of contamination would increase substantially, to 13 %, 35 %, and 36 % for BPA, DEHP, and MOHs, respectively. This indicates that a scenario where contamination of material is constrained, would only be efficient if a trade-off between material quantity (i.e. recycling rates) and material quality (i.e. contaminant content) is acceptable.

5.2.3 Remove (Technology development)

The last scenario took into consideration potential developments in technology employed in decontamination of the waste material stream for re-processing. Examples of such technologies in paper recycling are de-inking, cleaning, bleaching, etc. Higher average yields of decontamination of paper could arise either from conventional technologies covering larger share of recycled paper, or the improvement of technologies themselves. In case of paper as material in focus, effects of higher decontamination yields can range considerably. Results for SC2 in Figure 5-5, showed a range between 4 % and 78 % for BPA and MOHs, respectively. These results were proportional to the removal efficiencies achieved in paper re-processing, which ranged from 20 % for BPA (20 % refer to non de-inked paper, while BPA removal yields achieved in paper de-inking were 95 %) to 80 % for MOHs. These results suggested that in order to achieve significant reduction in contamination of a material cycle, significant improvements in the technology (hence, the decontamination yields) should be achieved. Similarly to the case discussed in section 5.2.2, improvements in the decontamination yield would also result in lower paper recycling yields, as higher fibre losses are expected [81]. Thus, also technology development may results in potential trade-offs between material quantity (i.e. yields of material re-processing) and quality (i.e. presence of chemical contaminants).

6 Conclusions

An approach for assessing the limitations for material recycling with respect to chemical contamination was developed and applied on paper and plastics as examples of recyclable materials. The approach was accompanied by quantitative assessment of chemical presence in the materials. In detail, the specific objectives of the work were addressed in the following manner:

- A household waste sampling campaign was designed and carried out. Detailed fractional composition of household waste paper (30 fractions) and plastics (9 fractions) was provided, indicating material complexity and the differences between fractional composition of residual and source-segregated waste flows.
- It was shown that paper may contain a large number of chemicals (approx. 10,000), the vast majority of which were harmless. Concerns over presence of chemicals in paper could be limited to a rather small number of hazardous chemicals (157), a subset of which (51) can be potentially problematic with respect to paper recycling.
- Concentrations of MOHs, phenols, phthalates, PCBs, and toxic metals in paper showed large variations across the chemical groups and across the paper fractions. Detailed fractional and chemical composition of waste paper allowed for identification of potential sources of chemical contaminants (e.g., BPA in receipts and PCBs in books). “Legacy” chemical contaminants were identified in both paper (i.e. PCBs) and plastics (i.e. BFRs), making product lifespan an important parameter on the way to “clean” material cycles.
- Chemicals may be added in a variety of steps throughout the lifecycle of paper products, with majority associated with paper printing and conversion. The presence of MOHs, BPA and DEHP showed potential for accumulation in the European paper cycle, whereas contaminant mitigation showed prevention of chemical use as the most effective way in contaminant elimination. Furthermore, potential trade-offs between material quantity (i.e. recycling rates) and quality (i.e. presence of contaminants) were pointed out.

7 Recommendations and perspectives

The issue of chemical contamination in material cycles calls for a combined effort, with active contributions from each of the "players" in the material value chain (i.e. stakeholders). The work provided here can serve as basis for decision making with the following recommendations towards the stakeholders involved:

- **Producers:** Based on the fact that prevention of chemical use was the most effective way in contaminant mitigation, suitability for material recycling should be considered in the earliest possible stages of product manufacturing. Optimally, product design should be adjusted in order to insure high quality products resulting in high quality recyclables. Additionally, transparency and reliability of data on use of chemicals in products and materials should be perceived.
- **Consumers:** As direct producers of household waste, consumers should follow the latest developments in sorting guidelines, allowing for a better quality of material being recovered for recycling.
- **Waste managers:** Waste sorting guidelines should be designed taking into consideration the latest data on presence of chemical contaminants in waste material fractions. This should be done in reflection on the input material quality (through collaboration with the producers) and material requirements (through collaboration with the recyclers).
- **Recyclers:** Sources of waste materials for recycling should be carefully selected, limiting the potential risks associated with presence of chemicals in materials. Traceability of materials recovered for recycling should be insured in order to assure re-processing in the materials and products of the appropriate quality. Chemical contamination should be considered when re-processing technologies are designed and implemented.
- **Legislators:** Increase in recycling rates of materials should be promoted, given the potential chemical contamination of a material is taken into account. Level "playing field" should be insured encouraging the competitiveness of secondary raw materials while minimizing the associated consumer and environmental risks.

To extend and develop further the findings of the present work, following suggestions are expressed in relation to perspectives for future research:

- In addition to paper and plastics, the approach proposed should be extended to **more material fractions** as to their content of chemicals resulting in potential contamination of material cycles. Contamination of fractions likely prioritized for recycling e.g., organic waste, food and food waste should also be considered in their synthetic (anthropogenic and natural) material cycles.
- Steps comprising material re-processing should be evaluated as to their **efficiency in material decontamination**. Such information would allow to quantify the potential removal of chemical contaminants in material re-processing creating solid basis for risk assessment related to production and use of products based on recycled materials. Coupled with material re-processing efficiency, this data would also allow for better assessment of potential trade-offs in quantity and quality of recycled materials.
- Due to increasing complexity of chemical constituents in materials, further targeted and **non-targeted chemical analyses** for material characterization should also take place in order to provide more data on presence of potentially "unknown" chemicals in materials.
- Based on the data provided in this work and future characterization of materials for recycling, material and chemical flow analyses should be linked with **risk assessments** providing a valuable contribution to monitor and control chemical flows in the increasingly circular economy.
- Finally, presence of chemical contaminants in materials and products should be considered when waste management options are evaluated from **system perspective** (e.g., life cycle assessment (LCA)).

8 References

[1] K. Pivnenko, T.F. Astrup, The challenge of chemicals in material cycles, Waste Manag. (2016), *In press*.

[2] G. Brundtland, M. Khalid, S. Agnelli, S. Al-Athel, B. Chidzero, L. Fadika, et al., Our Common Future (’Brundtland report'): Report for the World Commission on Environment and Development, United Nations, New York City, USA, 1987.

[3] WRAP, Environmental Benefits of Recycling An International Review of Life Cycle Comparisons for Key Materials in the UK Recycling Sector. Waste & Resource Action Programme (WRAP), Banbury, UK, 2006.

[4] L.S. Birnbaum, D.F. Staskal, Brominated flame retardants: cause for concern?, Environ. Health Perspect. 112 (2004) 9–17.

[5] ZELLCHEMING, Chemical Additives for the Production of Pulp & Paper, Ed. by ZELLCHEMING Technical Committee “Chemical Additives (CHAD)”, Deutscher Fachverlag Publisher, 2008.

[6] S. Al-Malaika, Perspectives in Stabilisation of Polyolefins, in: A.-C. Albertsson (Ed.), Adv. Polym. Sci., Springer Berlin Heidelberg, Berlin, Heidelberg, 2004: pp. 121–150. doi:10.1007/b13502.

[7] J. Muncke, Exposure to endocrine disrupting compounds via the food chain: Is packaging a relevant source?, Sci. Total Environ. 407 (2009) 4549–59. doi:10.1016/j.scitotenv.2009.05.006.

[8] T. Ekvall, A market-based approach to allocation at open-loop recycling, Resour. Conserv. Recycl. 29 (2000) 91–109. doi:10.1016/S0921-3449(99)00057-9.

[9] M. Biedermann, J.-E. Ingenhoff, M. Zurfluh, L. Richter, T. Simat, A. Harling, et al., Migration of mineral oil, photoinitiators and plasticisers from recycled paperboard into dry foods: a study under controlled conditions., Food Addit. Contam. Part A. Chem. Anal. Control. Expo. Risk Assess. 30 (2013) 885–98.

[10] M. Terasaki, H. Fukazawa, Y. Tani, M. Makino, Organic pollutants in paper-recycling process water discharge areas: first detection and emission in aquatic environment., Environ. Pollut. 151 (2008) 53–9. doi:10.1016/j.envpol.2007.03.012.

[11] A. Leung, Z.W. Cai, M.H. Wong, Environmental contamination from electronic waste recycling at Guiyu, southeast China, J. Mater. Cycles Waste Manag. 8 (2006) 21–33. doi:10.1007/s10163-005-0141-6.

[12] CEPI, Key Statistics. European Pulp and Paper Industry 2014, Confederation of European Paper Industries (CEPI). Brussels, Belgium, (2014).

[13] BIR, BIR global facts & figures. Recovered paper market in 2012, Bureau of International Recycling (BIR), Brussels, Belgium, (2012).

[14] PlasticsEurope, Plastics - the facts 2014/2015. An analysis of European plastics production, demand and waste data, Association of Plastics Manufacturers, Brussels, Belgium, (2015).

[15] EC, Proposal for a directive of the European Parliament and of the Council amending Directive 94/62/EC on packaging and packaging waste, COM (2015) 596. European Commission (EC), Brussels, Belgium, (2015).

[16] EC, Proposal for a directive of the European Parliament and of the Council amending Directive 2008/98/EC on waste, COM (2015) 595. European Commission (EC), Brussels, Belgium, (2015).

[17] S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): a review., Waste Manag. 29 (2009) 2625–43. doi:10.1016/j.wasman.2009.06.004.

[18] Nordtest, Municipal solid waste: Sampling and characterisation (No. NT ENVIR 001), Nordtest Method. Espoo, Finland, (1995).

[19] L. Petersen, P. Minkkinen, K.H. Esbensen, Representative sampling for reliable data analysis: Theory of Sampling, Chemom. Intell. Lab. Syst. 77 (2005) 261–277. doi:10.1016/j.chemolab.2004.09.013.

[20] EC, Regulation No 1907/2006 of the European Parliament and the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and, Off J Eur Union. (2006) L396: 1–849.

[21] A. Baun, E. Eriksson, A. Ledin, P.S. Mikkelsen, A methodology for ranking and hazard identification of xenobiotic organic compounds in urban stormwater., Sci. Total Environ. 370 (2006) 29–38. doi:10.1016/j.scitotenv.2006.05.017.

[22] T. Fierens, K. Servaes, M. Van Holderbeke, L. Geerts, S. De Henauw, I. Sioen, et al., Analysis of phthalates in food products and packaging materials sold on the Belgian market, Food Chem. Toxicol. 50 (2012) 2575–2583.

[23] T. Sipiläinen-Malm, K. Latva-Kala, L. Tikkanen, M.L. Suihko, E. Skyttä, Purity of recycled fibre-based materials., Food Addit. Contam. 14 (1997) 695–703.

[24] Miljøstyrelsen, Survey of chemical substances in paper handkerchiefs and toilet paper. Survey of chemical substances in consumer products No. 34, Miljøstyrelsen (Danish EPA), København, 2003.

[25] BMELV, Ausmaß der Migration unerwünschter Stoffe aus Verpackungsmaterialien aus Altpapier in Lebensmitteln, BMELV (German Federal Ministry of Food, Agriculture and Consumer Protection). Bonn, Germany, (2012).

[26] J.H. Petersen, L.K. Jensen, H.T. Jespersen, F. Sørensen, K. Schaumburg, Fødevareemballager af trykt papir og pap. Udvikling og validering af analysekoncept, DTU Fødevareinstituttet (Danish National Food Institute), (2013).

[27] M.F. Poças, J.C. Oliveira, J.R. Pereira, T. Hogg, Consumer exposure to phthalates from paper packaging: an integrated approach., Food Addit. Contam. Part A. Chem. Anal. Control. Expo. Risk Assess. 27 (2010) 1451–9.

[28] A.M. Vinggaard, W. Körner, K.H. Lund, U. Bolz, J.H. Petersen, Identification and Quantification of Estrogenic Compounds in Recycled and Virgin Paper for Household Use As Determined by an in Vitro Yeast Estrogen Screen and Chemical Analysis, Chem. Res. Toxicol. 13 (2000) 1214–1222.

[29] E.L. Bradley, U. Honkalampi-Hämäläinen, A. Weber, M.A. Andersson, F. Bertaud, L. Castle, et al., The BIOSAFEPAPER project for in vitro toxicity assessments: preparation, detailed chemical characterisation and testing of extracts from paper and board samples., Food Chem. Toxicol. 46 (2008) 2498–509.

[30] Miljøstyrelsen, Survey, emission and evaluation of volatile organic chemicals in printed matter. Survey of chemical compounds in consumer products No. 36, Miljøstyrelsen (Danish EPA), København, (2003).

[31] M.L. Binderup, G.A. Pedersen, A.M. Vinggaard, E.S. Rasmussen, H. Rosenquist, T. Cederberg, Toxicity testing and chemical analyses of recycled fibre-based paper for food contact., Food Addit. Contam. 19 Suppl (2002) 13–28.

[32] Miljøstyrelsen, Migration of bisphenol A from cash register receipts and baby dummies. Survey of chemical substances in consumer products No. 110, Miljøstyrelsen (Danish EPA), København, (2011).

[33] C. Liao, K. Kannan, Widespread occurrence of bisphenol A in paper and paper products: implications for human exposure., Environ. Sci. Technol. 45 (2011) 9372–9. doi:10.1021/es202507f.

[34] S. Biedermann, P. Tschudin, K. Grob, Transfer of bisphenol A from thermal printer paper to the skin., Anal. Bioanal. Chem. 398 (2010) 571–6.

[35] M. Gehring, L. Tennhardt, D. Vogel, Bisphenol A contamination of wastepaper, cellulose and recycled paper products, in: C.A. Brebbia, S. Kungolos, V. Popov, H. Itoh (Eds.), Waste Manag. Environ. II, WIT Press, (2004) 293–301.

[36] A. Ozaki, Y. Yamaguchi, T. Fujita, K. Kuroda, G. Endo, Chemical analysis and genotoxicological safety assessment of paper and paperboard used for food packaging., Food Chem. Toxicol. 42 (2004) 1323–37.

[37] S. Parry, Neutron activation analysis of recycled paper and board in contact with food, J. Radioanal. Nucl. Chem. 248 (2001) 143–147.

[38] L. Castle, A.P. Damant, C.A. Honeybone, S.M. Johns, S.M. Jickells, M. Sharman, et al., Migration studies from paper and board food packaging materials. Part 2. Survey for residues of dialkylamino benzophenone UV-cure ink photoinitiators., Food Addit. Contam. 14 (1997) 45–52.

[39] E. Storr-Hansen, S.C. Rastogi, Polychlorinated biphenyls and heavy metal levels in recycled paper for household use, Bull. Environ. Contam. Toxicol. 40 (1988) 451–456.

[40] C. Riber, C. Petersen, T.H. Christensen, Chemical composition of material fractions in Danish household waste., Waste Manag. 29 (2009) 1251–7.

[41] V.S. Rotter, T. Kost, J. Winkler, B. Bilitewski, Material flow analysis of RDF-production processes., Waste Manag. 24 (2004) 1005–21.

[42] A. Sturaro, R. Rella, G. Parvoli, D. Ferrara, F. Tisato, Contamination of dry foods with trimethyldiphenylmethanes by migration from recycled paper and board packaging., Food Addit. Contam. 23 (2006) 431–6. doi:10.1080/02652030500526052.

[43] M.-H. Zheng, Z.-C. Bao, B. Zhang, X.-B. Xu, Polychlorinated dibenzo-p-dioxins and dibenzofurans in paper making from a pulp mill in China, Chemosphere. 44 (2001) 1335–1337.

[44] G.L. LeBel, D.T. Williams, F.M. Benoit, Determination of chlorinated dibenzodioxins and dibenzofurans in selected paper products, Chemosphere. 23 (1991) 737–746.

[45] L. Castle, C.P. Offen, M.J. Baxter, J. Gilbert, Migration studies from paper and board food packaging materials. 1. Compositional analysis., Food Addit. Contam. 14 (1997) 35–44.

[46] SPIN, Substances in Preparations in Nordic countries (SPIN), http//195.215.202.233/DotNetNuke/default.aspx (Accessed Oct. 2013).

[47] KEMI, Overview of chemicals, Swedish Chemicals Agency http://kemi.se/en/Content/Statistics/Overview-of-chemicals/ (accessed March 2014), Sundbyberg, Sweden.

[48] Miljøstyrelsen, Kemikaliesubstitution i grafisk branche, Miljøproject Nr. 1354, Miljøstyrelsen (Danish EPA), Copenhagen, Denmark, (2011).

[49] Riskcycle, Risk-based management of chemicals and products in a circular economy at a global scale, Chemical Additive Database, Http//www.riskcycle.es (Accessed Novemb. 2013).

[50] EFSA, Report of ESCO WG on non-plastic Food Contact Materials, European Food Safety Authority (EFSA), Parma, Italy, (2012) 1–63.

[51] FDHA, Ordinance of the FDHA on Materials and Articles RS 817.023.21, Swiss Federal Department of Home Affairs (FDHA), Bern, Switzerland, (2005).

[52] EuPIA, Inventory list - version June 2012. Comprising of packaging ink raw materials applied to the non-food contact surface of food packaging. European Printing Ink Association, Brussels, Belgium, (2012).

[53] P.H. Brunner, H. Rechberger, Introduction, in: Pract. Handb. Mater. Flow Anal., CRC Press, (2004). doi:doi:10.1201/9780203507209.ch1.

[54] P.H. Brunner, H.W. Ma, Substance flow analysis an indispensable tool for goal-oriented waste management, J. Ind. Ecol. 13 (2009) 11–14. doi:10.1111/j.1530-9290.2008.00083.x.

[55] E. Müller, L.M. Hilty, R. Widmer, M. Schluep, M. Faulstich, Modeling metal stocks and flows: a review of dynamic material flow analysis methods., Environ. Sci. Technol. 48 (2014) 2102–13. doi:10.1021/es403506a.

[56] O. Cencic, H. Rechberger, Material flow analysis with software STAN, J. Environ. Eng. Manag. 18 (2008) 3–7.

[57] CEPI, CEPI sustainability report 2013. European Paper Industry - Advancing the bioeconomy, Confederation of European Paper Industries (CEPI). Brussels, Belgium, (2013).

[58] K. Breivik, A. Sweetman, J.M. Pacyna, K.C. Jones, Towards a global historical emission inventory for selected PCB congeners--a mass balance approach 2. Emissions, Sci. Total Environ. 377 (2007) 296–307. doi:10.1016/j.scitotenv.2007.02.026.

[59] US EPA, PCBs involvement in the pulp and paper industry. U.S. Environmental Protection Agency (EPA). Washington, DC, USA, (1977).

[60] P. Voogt, J.C. Klamer, U.A.T. Brinkman, Identification and quantification of polychlorinated biphenyls in paper and paper board using fused silica capillary gas chromatography, Bull. Environ. Contam. Toxicol. 32 (1984) 45–52. doi:10.1007/BF01607463.

[61] L.N. Vandenberg, M. V Maffini, C. Sonnenschein, B.S. Rubin, A.M. Soto, Bisphenol-A and the great divide: a review of controversies in the field of endocrine disruption., Endocr. Rev. 30 (2009) 75–95. doi:10.1210/er.2008-0021.

[62] JRC-IHCP, European Union Risk Assessment Report: 4, 4'-isopropylidenediphenol (Bisphenol-A), Eur. Union. 2008 (2008) 201–245. doi:10.2788/40195.

[63] NEA, Hazardous substances in plastic materials (TA-3017/2013), Norwegian Environment Agency (NEA). Oslo, Norway, (2013).

[64] J. Markarian, PVC additives – What lies ahead?, Plast. Addit. Compd. 9 (2007) 22–25. doi:10.1016/S1464-391X(07)70153-8.

[65] EC, Commission directive 2007/19/EC of 30 March 2007 amending Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with food and Council Directive 85/572/EEC laying down the list of simulants to be used for testing mig, Off. J. Eur. Union. L 91/17 (2007) 17–36.

[66] EU, Commision delegated directive (EU) 2015/863 of 31 March 2015 amending Annex II to Directive 2011/65/EU of the European Parliament and of the Council as regards the list of restricted substances, Off. J. Eur. Union. L137 (2015) 10–12.

[67] J. Jurewicz, W. Hanke, Exposure to phthalates: reproductive outcome and children health. A review of epidemiological studies., Int. J. Occup. Med. Environ. Health. 24 (2011) 115–141. doi:10.2478/s13382-011-0022-2.

[68] P. Kovacic, How dangerous are phthalate plasticizers? Integrated approach to toxicity based on metabolism, electron transfer, reactive oxygen species and cell signaling., Med. Hypotheses. 74 (2010) 626–8. doi:10.1016/j.mehy.2009.11.032.

[69] M. Alaee, P. Arias, A. Sjödin, A. Bergman, An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release., Environ. Int. 29 (2003) 683–9. doi:10.1016/S0160-4120(03)00121-1.

[70] D. Meironyté, K. Norén, A. Bergman, Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997., J. Toxicol. Environ. Health. A. 58 (1999) 329–41.

[71] A. Covaci, A.C. Gerecke, R.J. Law, S. Voorspoels, M. Kohler, N. V. Heeb, et al., Hexabromocyclododecanes (HBCDs) in the Environment and Humans: A Review, Environ. Sci. Technol. 40 (2006) 3679–3688. doi:10.1021/es0602492.

[72] EC, Directive 2003/11/EC of the European parliament and of the council of February 6 2003 amending for the 24th time Council Directive 76/669/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodip, Off J Eur Union OJ L. 16 (2003) 45–46.

[73] European Parliament, Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS), Off. J. Eur. Union. 54 (2011) 88–110. doi:10.1017/CBO9781107415324.004.

[74] N. V Heeb, W.B. Schweizer, M. Kohler, A.C. Gerecke, Structure elucidation of hexabromocyclododecanes--a class of compounds with a complex stereochemistry., Chemosphere. 61 (2005) 65–73. doi:10.1016/j.chemosphere.2005.03.015.

[75] N. V. Heeb, W. Bernd Schweizer, P. Mattrel, R. Haag, A.C. Gerecke, P. Schmid, et al., Regio- and stereoselective isomerization of hexabromocyclododecanes (HBCDs): Kinetics and mechanism of γ- to α-HBCD isomerization, Chemosphere. 73 (2008) 1201–1210. doi:10.1016/j.chemosphere.2008.07.045.

[76] V. Goodship, Introduction to Plastics Recycling, Second Edi, Smithers Rapra Press, (2007).

[77] EC, Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain directives, Off. J. Eur. Union. L312 (2008) 3–30. doi:2008/98/EC.; 32008L0098.

[78] L. Kong, A. Hasanbeigi, L. Price, Assessment of emerging energy-efficiency technologies for the pulp and paper industry: A technical review, J. Clean. Prod. 122 (2016) 5–28. doi:10.1016/j.jclepro.2015.12.116.

[79] M. Terasaki, F. Shiraishi, T. Nishikawa, J.S. Edmonds, M. Morita, M. Makino, Estrogenic Activity of Impurities in Industrial Grade Bisphenol A, Environ. Sci. Technol. 39 (2005) 3703–3707. doi:10.1021/es048932g.

[80] J.R. Peeters, P. Vanegas, L. Tange, J. Van Houwelingen, J.R. Duflou, Closed loop recycling of plastics containing Flame Retardants, Resour. Conserv. Recycl. 84 (2014) 35–43. doi:10.1016/j.resconrec.2013.12.006.

[81] E. Hanecker, C. Ewald, A. Kersten, Mineralölentfernung aus Altpapierstoffen, in: Work. ”Mineralöl Leb., München, (2012).

9 Papers

I Edjabou M., Jensen M., Götze R., **Pivnenko K.**, Petersen C., Scheutz C., Astrup T.F. (2015) Municipal solid waste composition: Sampling methodology, statistical analyses, and case study evaluation, *Waste Management* (36), 12-23

II **Pivnenko K.**, Eriksson E., Astrup T.F. (2015) Waste paper for recycling: Overview and identification of potentially critical substances, *Waste Management* (45), 134-142

III **Pivnenko K.**, Olsson M., Götze R., Eriksson E., Astrup T.F. (2016) Quantification of chemical contaminants in the paper and board fractions of municipal solid waste, *Waste Management* (51), 43-54

IV **Pivnenko K.**, Pedersen G.A., Eriksson E., Astrup T.F. (2015) Bisphenol A and its structural analogues in household waste paper, *Waste Management* (44), 39-47

V **Pivnenko K.,** Eriksen M.K., Martín-Fernández J.A., Eriksson E., Astrup T.F. (2016) Recycling of plastic waste: presence of phthalates in plastics from households and industry, *Waste Management*, In press

VI **Pivnenko K.**, Granby K., Eriksson E., Astrup T.F. Recycling of plastic waste: Screening for brominated flame retardants, *Manuscript*

VII **Pivnenko K.**, Laner D., Astrup T.F. Material cycles and chemicals: Dynamic material flow analysis of contaminants in paper recycling, *Submitted*

In this online version of the thesis, **Paper I-VII** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Bygningstorvet, Building 115, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk.

The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within six sections: Water Resources Engineering, Water Technology, Urban Water Systems, Residual Resource Engineering, Environmental Chemistry and Atmospheric Environment.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

Department of Environmental Engineering
Technical University of Denmark

DTU Environment
Bygningstorvet, building 115
2800 Kgs. Lyngby
Tlf. +45 4525 1600
Fax +45 4593 2850

www.env.dtu.dk